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NSWC TR 86-296

AD-A181 040

SAFETY CHARACTERISTICS OF LITHIUM PRIMARY AND SECONDARY BATTERY SYSTEMS

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CONTRACT NO. N60921-84-C-0207
JULY 1986

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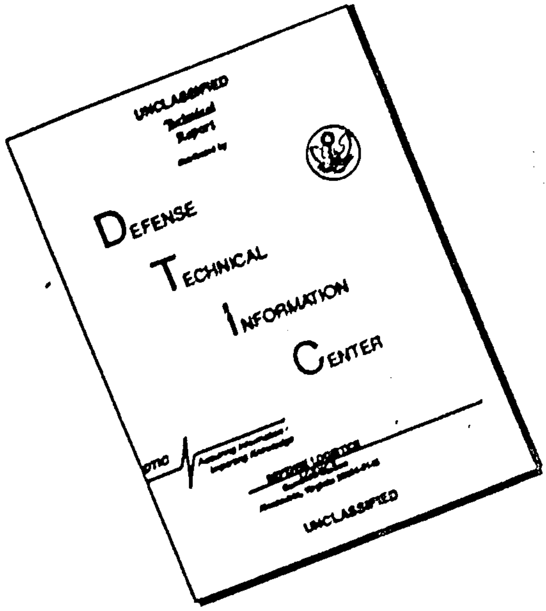

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER NSWC TR 86-296	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) SAFETY CHARACTERISTICS OF LITHIUM PRIMARY AND SECONDARY BATTERY SYSTEMS Formulation Of A Lithium Battery Safety Matrix		5. TYPE OF REPORT & PERIOD COVERED Final; Oct 84 to Jul 86 6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Robert M. Murphy R. Frank Bis James A. Barnes William V. Zajac Patrick B. Davis		8. CONTRACT OR GRANT NUMBER(s) N60921-84-C-0207
9. PERFORMING ORGANIZATION NAME AND ADDRESS Advanced Battery Group 269 Westwood Road Lancaster, NY 14086		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS Naval Surface Weapons Center (R33) 10901 New Hampshire Ave. Silver Spring, MD. 20903-5000		12. REPORT DATE July 1986 13. NUMBER OF PAGES 150
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report) UNCLASSIFIED 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution is unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Primary Lithium Systems	Short Circuit	Safety Devices	Design
Secondary Lithium Systems	Overdischarge	Transportation	
NAVSEANOTE 9310	Charging/Overcharging	Storage	
Safety	Incineration	Disposal	
Hazards	Failure Mechanisms	Manufacturers	

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

A study was conducted to assess the safety characteristics for both primary and secondary lithium electrochemical systems. Of particular interest is the behavior of specific cell designs of these systems when subjected to the electrical and thermal abuse test procedures prescribed in NAVSEANOTE 9310. These abusive tests include short circuit, forced overdischarge, charge, and incineration. The main intent of the report is the formulation of a lithium battery safety matrix wherein certain electrochemical systems, cell

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S/N 0102-LF-014-6601

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20. (cont.)

designs, or cell types which have exhibited exceptionally safe characteristics under abusive conditions may be exempt from some or all of the NAVSEANOTE 9310 test procedures. The focus of the study concerns the six major primary lithium systems of most interest to the U.S. military establishment: Li-CuO, Li-MnO_2, Li-$(CF_x)_n$, Li-SO_2, Li-SO_2Cl_2, and Li-$SOCl_2$. Other lithium primaries included are: the Li-Aqueous electrolyte systems, Li-CuS, Li-I_2, the Li-Iron Sulfide systems, the Li alloy-thermal batteries, and the Li-V_2O_5 based systems. Secondary lithium systems included in this study are: Li-Cl_2, Li-MoS_2, and Li-TiS_2. Chapter 2 details the electrochemical/chemical, mechanical, thermal, and electrical safety methods, designs, or devices which serve to prevent thermal runaway, venting, or rupture. Current policies, regulations, and practices relative to the safe transport, storage, and disposal of lithium batteries are given in Chapter 3.

FOREWORD

A study was conducted to assess the safety characteristics for both primary and secondary lithium electrochemical systems. Of particular interest is the electrical and thermal abuse test procedures prescribed in NAVSEANOTE 9310. These abusive tests include short circuit, forced overdischarge, charge, and battery safety matrix wherein certain electrochemical systems, cell designs, or cell types which have exhibited exceptionally safe characteristics under abusive conditions may be exempt from some or all of the NAVSEANOTE 9310 test procedures. The focus of the study concerns the six major primary lithium systems of most interest to the U.S. military establishment: Li-CuO, Li-MnO_2, Li-$(CF_x)_n$, Li-SO_2, Li-SO_2Cl_2, and Li-$SOCl_2$. Other lithium primaries included are: the Li-Aqueous electrolyte systems, Li-CuS, Li-I_2, the Li-Iron Sulfide systems, the Li-alloy thermal batteries, and the Li-V_2O_5 based systems. Secondary lithium systems included in this study are: Li-Cl_2, Li-MoS_2, and Li-TiS_2. Chapter 2 details the electrochemical/chemical, mechanical, thermal, and electrical safety methods, designs, or devices which serve to prevent thermal runaway, venting, or rupture. Current policies, regulations, and practices relative to the safe transport, storage, and disposal of lithium batteries are given in Chapter 3.

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CHAPTER 1

INTRODUCTION AND BACKGROUND

Primary lithium battery systems were developed within the past fifteen to twenty years. Compared to many conventional systems, these lithium systems offer the user substantial increases in both gravimetric and volumetric energy densities, high cell voltages with good voltage regulation, operation over a wide range of temperatures, and excellent storability characteristics. The first successful primary lithium system was invented by Maricle and Mohns[1] at American Cyanimid and utilized sulfur dioxide as the active cathode material. Early cell designs employed a spirally wound cell structure with a carbon positive electrode current collector, a cylindrical steel can, and a crimp seal. The electrolyte solution contained lithium bromide in a mixture of propylene carbonate and acetonitrile to which the sulfur dioxide was added. Following its introduction to the market in early 1970, the lithium-sulfur dioxide system quickly became a promising power source alternative to the many non-lithium battery systems available to the military and space community.

The widespread use of the lithium-sulfur dioxide battery system was limited by concerns relating to the safety and hazard characteristics exhibited by cells or batteries exposed to electrical, mechanical, and thermal abuse conditions. The first report describing the hazards associated with lithium-sulfur dioxide cells was given by Wilburn[2] in 1972. Wilburn found that cells exposed to short circuit conditions experienced thermal runaways resulting in cell ruptures and fires. Later, Warburton[3] tested lithium-sulfur dioxide, lithium-copper (II) sulfide, and lithium-polycarbon monofluoride C sized, spirally wound cells to determine each system's suitability for ordnance applications. Warburton found that lithium-sulfur dioxide and lithium-polycarbon monofluoride cells with no vent mechanisms exploded violently after reaching the melting point of lithium when discharged under loads of 0.1 and 0.25 ohm but did not explode when discharged under a load of 0.01 ohm, resulting in cell temperatures of less than

100°C. The lithium-copper (II) sulfide cells did not explode under any of the discharge conditions. Exposure of non-vented cells to thermal abuse conditions resulted in violent explosions for all three cell systems. Warburton also tested lithium-sulfur dioxide cells fitted with a vent mechanism consisting of a frangible metal disc. All cells vented at temperatures of 100°C when subjected to the load and thermal abuse described above.

The first formal safety test program for lithium-sulfur dioxide D cells and batteries (BA-5590/U, 24V, ten D cells in series) was devised by Brooks[4] at ECOM (presently the U.S. Army Electronics Research and Development Command [ERADCOM], Fort Monmouth, N.J.). All D cells tested were of the spirally wound, crimp seal design and contained vent mechanisms. Fresh and partially discharged single cells were subjected to seven abuse tests: short circuit (0.01 ohm), increasing load (discharge at increasingly higher rates until the cell deactivated or vented), hot plate (temperature increased at a rate of 20°F (11°C) per minute until the cell deactivated or vented), cell deformation test (crushing), dynamic environment (shock or vibration), case rupture (penetration by a high speed drill), and incineration (localized heating until the cell deactivated or vented). The BA-5590/U batteries were also subjected to the short circuit, increasing load, and hot plate tests described above. The batteries, however, were also subjected to salt and fresh water immersion tests followed by discharge at the five hour rate and to forced overdischarge testing at the five hour rate. None of the single cell tests resulted in fires or explosions for any of the cells supplied by Mallory (Duracell, Inc.) or Power Conversion, Inc. One battery exhibited an explosion and fire when subjected to the forced overdischarge test. After enlarging the vent structure on the D cells comprising the battery, subsequent forced overdischarge testing resulted in venting with no instances of cell rupture or fire.

Simultaneous investigations conducted by Auburn, French, Lieberman, Shah, and Heller[5] at GTE Laboratories, by Blomgren and Kronenberg[6,7] at Union Carbide Corporation, and by Behl, Christopulos, Ramirez, and Gilman[8] at the U.S. Army Electronics Command, Fort Monmouth led to the development of several lithium-oxyhalide systems which included lithium-thionyl chloride, lithium-sulfuryl chloride, and lithium-phosphoryl chloride. Earlier work by Gabano[9] at SAFT

focussed on the use of a halogen, either bromine or chlorine, as the active cathode material dissolved in a solution comprised of thionyl chloride as the solvent with lithium tetrachloroaluminate as the electrolyte salt. Of the several possible lithium-oxyhalide systems investigated, only the lithium-thionyl chloride cell which incorporated bromine chloride as a second cathode component was developed and commercialized by Krehl, Liang, and Danner[10] at Electrochem Industries. A second lithium-sulfur oxyhalide system utilizing chlorine in sulfuryl chloride as the active cathode materials was developed at Electrochem Industries by Murphy, Liang, and Bolster[11,12] in late 1980.

As the lithium-sulfur dioxide and lithium-thionyl chloride systems found acceptance for several military and commercial applications, safety related incidents involving ventings, fires, and explosions have occurred. Specific causes for the accidents include electrical abuse (e.g., short circuiting, forced overdischarge, charge, and high rates of discharge leading to thermal runaway conditions), thermal events (exposure to high temperature environments and the development of internal short circuits), mechanical abuse (subjecting cells to severe shock and vibration regimen, puncture, crushing, and restriction of cell venting mechanisms or improper vent operation), and chemical side reactions (attack on the glass to metal seal and terminal pin material as well as the production of highly reactive or unstable species). Table 1 lists the safety related incidents from 6 October 1974 to 31 December 1984 as compiled by Bowers,[13] Bis and Barnes,[14] and Bis and Zajac.[15] It is important to note that many of the citations given in Table 1 derive from several independent sources through telephone conversations, meetings, or non-technical news media. In view of the above, several cited incidents may not be as highly rigidly documented to completely satisfy the technical community. However, in view of the fact that the list has been repeatedly shown publicly, the data given appear to be substantially accurate. A summary of the data is given below:

1. All of the safety related incidents involved lithium-sulfur dioxide, lithium-thionyl chloride, or lithium-chlorine in sulfuryl chloride cells or batteries.
2. All of the incidents from October 1974 to November 1974 involved batteries using lithium-sulfur dioxide cells with the crimp seal design.

TABLE 1. LITHIUM BATTERY SAFETY INCIDENTS AS COMPILED BY THE LITHIUM SYSTEMS SAFETY GROUP AT NSWC

DATE	LOCATION	VENTING HEATING LEAKING	FIRE	EXPLOSION RUPTURE BURST	COMMENTS
OCT 1974	Miami		X		
OCT 1974	Chicago		X		
NOV 1974	Chicago			X	
NOV 1974	Seattle		X		
AUG 1976[a]	Unspecified		X	X	
AUG 1976	Hill AFB			X	personal injury
DEC 1976	Ft. Monmouth	X		X	
FEB 1977	Costa Mesa, CA		X		
FEB 1977[b]	Plymouth Meeting, PA			X	personal injury
MAR 1977[c]	Braintree, MA		X	X	
JUL 1977[d]	Norway	X			personal injury
JUL 1977	Langley, VA			X	
JUN 1979	Bermuda	X			
JUL 1979	Horsham, PA			X	
SEP 1979	Bermuda	X	X	X	personal injury
SEP 1979	High Seas			X	
JUN 1980	Norway		X	X	
JAN 1981	Houston			X	personal injury
JAN 1981	Ft. Bragg	X			
JAN 1981	Ft. Sill	X			
FEB 1981	Ft. Mead		X	X	

TABLE 1. (Cont.)

DATE	LOCATION	VENTING HEATING LEAKING	FIRE	EXPLOSION RUPTURE BURST	COMMENTS
APR 1981	Ft. Huachuca	X			
NOV 1981	Germany (FDR)		X	X	
NOV 1981	China Lake, CA			X	
FEB 1982	NWSC, Crane, IN			X	
FEB 1982	NWSC, Crane, IN			X	
OCT 1982	Anaheim, CA			X	
FEB 1983	Clarence, NY			X	personal injury
MAR 1983	NSWC, White Oak, MD	X			
MAR 1983	Alaska			X	personal injury
APR 1983	Barbers Point, HI	X	X		
MAY 1983	Brunswick NAS, ME	X	X		
MAY 1983	Out of country			X	
JUN 1983	Norton AFB			X	
AUG 1983	Ft. Carson	X			
AUG 1983	Ft. Bragg			X	
SEP 1983[e]	Texas Instruments	X			
OCT 1983	Beirut			X	
OCT 1983	Beirut			X	
OCT 1983	Ft. Pickett			X	
OCT 1983	Camp Lejeune			X	
OCT 1983	Panama	X			
NOV 1983	Granada			X	
DEC 1983	Beirut			X	
DEC 1983	Beirut	X			
DEC 1983	Elgin AFB			X	
DEC 1983	Ft. Gordon	X			
DEC 1983	Camp Lejeune	X			
JAN 1984	Ft. Bragg	X			
FEB 1984[e]	Marine AMP Unit			X	
FEB 1984	Ft. Bragg			X	

TABLE 1. (Cont.)

DATE	LOCATION	VENTING HEATING LEAKING	FIRE	EXPLOSION RUPTURE BURST	COMMENTS
MAR 1984	Camp Lejeune	X			
JUN 1984	NWSC, Crane, IN	X			
JUL 1984[e]	Cincinnati Electronics			X	
AUG 1984[e]	White House Comm. Agency	X			
AUG 1984[e]	White House Comm. Agency	X			worldwide alert
SEP 1984	NSWC, White Oak, MD	X			
NOV 1984	NOSC, San Diego	X			
NOV 1984[e]	Marine Corps Communication Electronics School	X			

NOTES:

[a] Lithium battery exploded during a test of slide raft equipment on a commercial aircraft (F.M. Bowers,[13] original report: telecon between P. Neuman, FAA Systems and Equipment Branch AFS-130, and F.M. Bowers, Code CR-33 of NSWC, 2 Aug 1977).

[b] Location previously reported to be Minneapolis, MN,[14] original report (Bowers[13]) indicates Plymouth Meeting, PA.

[c] Location previously reported as Waynard, MA,[14] original report (Bowers[13]) indicates Braintree, MA.

[d] Original reference (Bowers,[13] ref. 27) indicates the date of occurrence was Fall, 1976 (Dept. of Army R and D News, AST-2660 P-107-76, p. 23, 19 Nov (1976)).

[e] Locations unspecified, data supplied to NSWC by U.S. Army sources.

These were used as the power sources for the Emergency Locator Transmitter (ELT) aboard commercial and private aircraft.[13] Following an investigation by the Federal Aviation Administration, it was recommended that properly fused ELT batteries be comprised of vented, hermetically sealed cells.

3. The most serious accident resulted in a loss of life and injuries to two nearby personnel when a discharged 10,000 Ah lithium-thionyl chloride cell exploded at Hill Air Force Base in August 1976.[13]

4. No personal injuries have been reported for the period of March 1983 to June 1985.[15]

The responsibilities and procedures for lithium battery handling, disposal and safety within the U.S. Navy are set forth in NAVSEANOTE 9310.[16] The major premise of this document specifically requires that lithium batteries be considered as power supplies for U.S. Navy applications only when no other power sources can meet the application requirements of the end use item. In accordance with the above referenced document, the lithium batteries and the end use items containing lithium batteries are subjected to extensive design review processes and testing prior to the introduction of the devices to the general Fleet. The technical authority for the lithium battery safety program for the Navy is the Naval Sea Systems Command, NAVSEA 06H. The lead laboratory for the program is the Naval Surface Weapons Center (NSWC), Electrochemistry Branch, Code R33.

Formerly, three abuse tests were employed by the U.S. Navy to evaluate and assess the safety characteristics of lithium batteries in lithium powered end use items:

1. Constant current discharge and voltage reversal test - three properly instrumented (thermocouples and pressure transducer) end items are discharged under constant current conditions using a DC power supply. The internal fusing devices are bypassed and the discharge is performed at current and voltage levels equal to the value of the battery pack fuse and the open circuit voltage of the battery pack, respectively. After the battery voltage reaches zero volts, the discharge is to be continued into voltage reversal at the fuse current level until 1.5

times the advertized capacity of the battery pack has been attained. Voltage, temperature, and pressure are continuously monitored. This test simulates the electrical abuse condition observed when the capacities of one or more cells in series are less than the capacities of the majority of cells. The voltage reversal condition also arises when the operational requirements for a battery pack necessitates the use of multiple voltage tapping (i.e., some cells in a series string will become depleted before other cells in the same string).

2. Short circuit test - three properly instrumented (thermocouples and pressure transducer) end items are short circuited through a resistive load of 0.01 ohm for a minimum period of 24 hours. All internal electrical and thermal protective devices are to be bypassed. Voltage, current, pressure, and temperature are continuously monitored and recorded. This test represents perhaps the most common hazard occurrence when the unit is in practical Fleet deployment. The short circuit may therefore occur when the battery terminals or lead wires contact conductive surfaces such as metal shelving, tools, or the surface of the end use item (resulting from severe shocks, vibrations, or mechanical rupture of the end item by, for example, a fork lift).

3. High temperature exposure - three properly instrumented (thermocouples and pressure transducer) end items are heated at a constant rate of 20°C per minute until a limiting temperature of 500°C is achieved. Voltage, pressure, and temperature are continuously monitored and recorded. Though this test does indeed characterize the battery behavior during an actual, on-board fire, the primary purpose of this test is the determination of the hazards characteristics arising from a massive internal short circuit (partial or complete separator failure, lead contact, or dislodgement of the cell separator as a result of shock, vibration, or spin environments).

Many U.S. Navy applications require higher current levels or longer operational lifetimes than could be provided by a battery containing a single series string of cells at a specified operational voltage. Since most lithium cells currently manufactured in the United States are restricted to sizes no larger than the DD size, it is generally not practical, from an economic

standpoint, for defense contractors to expend the funds for the development of large custom cells. As a result, some end items could contain batteries of two or more parallel strings of cells in order to meet the required levels of performance. There exists the possibility, therefore, that one or more of the parallel strings could induce a charging mode with a weaker (depleted or partially depleted) string of cells within the battery pack if diode protection is not provided, is bypassed, or has failed. A charging mode will also occur in the event of diode failure in a battery pack used as a reserve power supply to a main power supply, as in the case for some applications aboard U.S. Navy aircraft. The occurrence of a charging mode could lead to a hazardous condition, particularly in the case of lithium batteries. In view of the above, a fourth safety test procedure was incorporated in NAVSEANOTE 9310 to evaluate the safety characteristics associated with electrically charging a battery which either consists of parallel strings of cells or is to be used as a backup power source to a main power supply:

4. Charging test - three properly instrumented (thermocouples and pressure transducer) end items are discharged under constant current conditions using a DC power supply. The internal electrical fusing devices are bypassed and the discharge is performed at a current level equal to the fuse value until at least 50% of the battery capacity has been removed. The battery is allowed to stand under open circuit conditions for a minimum period of 72 h. The battery is then charged at a current equal to the fuse value to 100% of the battery's capacity. The voltage of the DC power supply is limited either to the open circuit voltage of the battery pack or to the voltage of the main power supply, whichever is greater. Voltage, current, temperature, and pressure are continuously monitored and recorded.

NAVSEANOTE 9310 also includes a fifth test to determine the effectiveness of the electrical safety devices in preventing the occurrence of ventings, fires, or ruptures when the battery is subjected to a constant current discharge and reversal test regime:

5. Electrical safety device test - three properly instrumented

(thermocouples and pressure transducer) end items are discharged under constant current conditions using a DC power supply. All electrical safety devices are in place and operational. The discharge is performed at current and voltage levels equal to 0.8 to 0.9 the battery fuse value and the open circuit voltage of the battery, respectively. After the battery voltage reaches zero volts, the discharge is continued into voltage reversal at the above current level until 1.5 times the advertized capacity of the battery pack has been attained. Voltage, temperature, and pressure are to be continuously monitored and recorded. No venting of any kind is allowed for this test.

It is important to note that specialized testing procedures or adaptations to the above tests must be developed for specific primary lithium battery designs, secondary lithium systems, and some fused salt lithium batteries under consideration for U.S. Navy and other U.S. military organizations. For example, lithium reserve batteries may be tested to determine the safety characteristics attendant with either inadvertent activation while the terminals are short circuited or exposure to incineration conditions in the non-activated state. The latter scenario could result in the introduction of a soluble cathode material (e.g., thionyl chloride) into a cell stack containing molten lithium. One such application requiring a reserve lithium-thionyl chloride battery is the Rockwell EX 9 antisubmarine warfare target vessel. Other primary lithium systems requiring special testing consideration include the Li/H_2O and Li/H_2O_2 (hydrogen explosion hazard) and the $Li(alloy)/FeS_2$ thermal battery (pyrotechnics). The charge testing regime as given above must be expanded to determine the safety characteristics for secondary lithium systems during excessive overcharge conditions, the effect of various charging methods, and possible thermal runaway conditions incurred during overcharge at rates or voltages above those recommended. Fused salt systems necessarily require high operational temperatures. The accidental rupture of an active thermal battery unit in contact with a water supply could not only result in a fire but also could cause a steam explosion, an explosion of trapped gases, or the release of toxic materials as a consequence of a fused salt-water reaction.[17] However, it is important to note that the construction for thermal batteries is extremely rugged. As a result, thermal batteries should be abuse resistant to mechanical

rupture. It should also be mentioned that the exposure of the contents of any lithium cell to a water supply could also result in a lithium fire. Tests indicate, moreover, that secondary fires caused by lithium batteries are best fought with copious amounts of water.

Perhaps the most successful lithium battery program in the U.S. military has been conducted through the close cooperation of the personnel at the U.S. Army Electronics Research and Development Command, Fort Monmouth and the lithium-sulfur dioxide battery manufacturers. At the present time, the U.S. Army fields nine types of lithium-sulfur dioxide batteries[18]: the BA-5567/U, a low rate (to 1A) single cell unit; the BA-5847/U, a medium rate (1 to 2A) series connected two cell unit; the BA-5599/U and BA-5600/U, medium rate (1 to 2A) series connected three cell units; the BA-5588/U, a low rate (to 1A) series connected five cell unit; the BA-5598/U, a medium rate (1 to 2A) series connected five cell unit with provision for single cell voltage tapping; the BA-5513/U, a medium rate (1 to 2A) unit comprised of two parallel strings of five cells in series; the BA-5557/U, a low rate (to 0.7A) unit comprised of two series connected strings of five cells each; and the BA-5590/U, a medium rate (1 to 2A) unit comprised of two series connected legs of five cells in series. The BA-5567/U single cell battery is not protected by an electrical fuse, a thermal fuse, or by a blocking diode. All other batteries are protected by time delay, non-replaceable electrical fuses at current levels of: 0.8A (BA-5557/U), 1A (BA-5588/U), and 2.25A (BA-5847/U, BA-5599/U, BA-5600/U, BA-5598/U, BA-5513/U, and BA-5590/U). Thermal fuses are positioned in the geometric center of the battery, between any two adjacent cells, or in the center of a cluster of cells.[18] Amendment 3 of MIL-B-49430 (ER) also requires the incorporation of blocking diodes to prevent the inadvertent electrical charging of the battery or string of cells within the battery by an external power source or by a second string of cells, respectively.

The procurement of U.S. Army lithium-sulfur dioxide batteries is governed by MIL-B-49430 (ER), its amendments, and other specifications included in the procurement contract. MIL-B-49430 (ER) requires that the manufacturer submit Quality Conformance Test Reports to show that the cells or batteries have passed performance, safety, storability, or environmental testing (e.g., capacity, voltage reversal, vent operation, leakage, short circuit, thermal and electrical

fuse operation, voltage delay, shock and vibration, etc.). The reports must also certify that the water content of the sulfur dioxide electrolyte solution in a cell shall not exceed 1000 parts per million by weight and that the coulombic ratio of lithium to sulfur dioxide is 1.0 ± 0.1 (i.e., "balanced" lithium-sulfur dioxide cells). The low water content and balanced cell design are directly related to the safety characteristics of the battery units. Excess moisture results in the production of hydrogen with an attendant increase in internal pressure and the separation of portions of the lithium anode from the current collector.[19] The absence of available lithium in cells experiencing near voltage reversal conditions also avoids the direct reaction of finely divided lithium with acetonitrile. This reaction often results in the production of lithium cyanide and methane gas in the absence of sulfur dioxide for non-stoichiometrically balanced cells (i.e., excess lithium) experiencing voltage reversal conditions.[20] The procurement contract requires that two percent of the weekly production lot be submitted to the government for independent testing. These tests include chemical analyses to verify both the water content and the coulombic ratio, performance testing, and long term storage tests.

The safety record for U.S. Army lithium-sulfur dioxide batteries was recently discussed by Berger.[21] Twenty-seven failures in 664,000 batteries (approximately 4.4×10^6 cells) delivered to storage depots were reported for the period of 1979 to October 1984. It is important to note that these statistics relate to safety incidents in the field and do not reflect routine supply problems (e.g., leakage or venting during storage, corrosion of molybdenum terminal pins, poor welds, etc.).[19] Nonetheless, the safety record for U.S. Army lithium-sulfur dioxide batteries has been compared to that for the zinc-manganese dioxide (alkaline) cell system.[21] The most recent U.S. Army data[19] (April, 1985) indicates that, of approximately thirty to forty safety related incidents, eleven were of sufficient force to rupture the battery container, thereby causing some equipment damage. The worst personnel injury reported for any of these safety incidents was an acid burn on a soldier's hand.[19]

In contrast to the use conditions described above for the U.S. Army lithium-sulfur dioxide batteries, many U.S. Navy applications require lithium-sulfur dioxide batteries to be discharged at high rates, often many times in

excess of those normally recommended by the manufacturer. For example, a lithium-sulfur dioxide battery comprised of twelve high rate, non-stoichiometrically balanced D cells was discharged at a constant current of 21A.[22] The test was conducted to determine whether the battery could meet both the performance and safety requirements for the Counter Arm Decoy System. In view of such requirements, the probability for safety related incidents involving such end items deployed in the Fleet could be higher than that experienced by the U.S. Army. It can be seen, therefore, that it is necessary for the U.S. Navy to evaluate the total system safety as specified in NAVSEANOTE 9310. As a result of this approach as well as particular attention to specific use conditions for the end item, the probability for safety incidents within the U.S. Navy is reduced significantly. This evaluation results in acceptable safe limits of use.

STUDY APPROACH

Detailed investigations have been conducted to assess and improve the safety characteristics of such lithium primary electrochemical systems as lithium-sulfur dioxide, lithium-thionyl chloride and lithium-sulfuryl chloride. Many such studies have resulted in the development of safer, more reliable power sources which are presently in use in several U.S. military applications. One specific intent of this study is to determine, correlate, and assess the safety characteristics for the state-of-the-art lithium-sulfur dioxide, lithium-thionyl chloride and lithium-sulfuryl chloride systems relative to NAVSEANOTE 9310. Though the above primary systems constitute the major interest for present U.S. military applications, several primary and secondary lithium systems are commercially available which possess operational characteristics which meet or exceed the requirements for U.S. military applications. As the number and usage of lithium primary and secondary electrochemical systems increase, testing in accordance with NAVSEANOTE 9310 will require the expenditure of large amounts of time, the acquisition of sophisticated test equipment, and the addition of technical personnel. The ultimate goal of this study is the determination of the safety characteristics for several lithium primary and secondary systems relative to NAVSEANOTE 9310 and the evaluation of these systems as regards their utilization in the Fleet without having to undergo the formal test program of NAVSEANOTE 9310.

Prime importance is placed upon the safety issues of primary and secondary lithium systems as they directly relate to the test procedures of NAVSEANOTE 9310. The scope of the work, however, is not limited to the abuse testing of NAVSEANOTE 9310 but extends to further include specific safety issues intrinsic to cell design, energy content, additives, etc. In addition, the following would also be of interest to more completely characterize the safety features for the systems selected for this study: mechanical abuse testing (e.g., crushing, penetration, shock and vibration, etc.) and specialized thermal abuse testing (e.g., localized heating, temperature cycling, etc.).

Table 2A shows the major lithium primary systems determined to be of the most interest to U.S. military organizations. The major emphasis of this study focusses on the characteristics of these systems for present and near term military applications. Less emphasis is placed upon the primary lithium systems given in Table 2B. In most instances, these systems represent special application requirements (e.g., the lithium thermal batteries and the aqueous electrolyte systems). In addition, significantly less information is available relative to the performance and safety characteristics for such systems. Table 2C gives examples of secondary lithium systems, some of which have reached the advanced development stage but are not fully commercialized at this time. There exists the definite possibility that several secondary systems will be of importance to the military in a variety of applications. Consequently, relevant data for these systems are included in this study with the intention that the data be revised once the systems become commercially available.

In order to accomplish the objectives of the study, a number of data sources were utilized to obtain as much relevant information regarding the safety and operational characteristics for each lithium system. The nature and extent of each source is given below:

1. Manufacturer's survey - Several United States and foreign lithium battery manufacturers, commercial users, and personnel at a disposal facility were contacted to obtain relevant performance and safety data generated by the research and development, reliability, or applications

TABLE 2. PRIMARY AND SECONDARY ELECTROCHEMICAL SYSTEMS EVALUATED IN THIS STUDY

A. Major Primary Lithium Battery Systems

1. Lithium - Copper (II) Oxide Based Systems, CuO and $Cu_4O(PO_4)_2$
2. Lithium - Manganese Dioxide
3. Lithium - Polycarbon Monofluoride
4. Lithium - Sulfur Dioxide
5. Lithium - Sulfuryl Chloride Based Systems, SO_2Cl_2 and Cl_2 in SO_2Cl_2
6. Lithium - Thionyl Chloride Based Systems, $SOCl_2$ and BrCl in $SOCl_2$

B. Other Primary Lithium Battery Systems

1. Lithium - Aqueous Electrolyte Systems, O_2, H_2O_2, Ag_2O_2, and H_2O
2. Lithium - Copper (II) Sulfide
3. Lithium - Iodine
4. Lithium - Iron Sulfide Systems, FeS and FeS_2
5. Lithium (Lithium Alloy) - FeS_2 Thermal Battery Systems
6. Lithium - Vanadium Pentoxide Based Systems, V_2O_5 and $AgVO_x$

C. Secondary Lithium Battery Systems

1. Lithium - Chlorine
2. Lithium - Molybdenum Disulfide
3. Lithium - Titanium Disulfide

engineering departments of each organization. Table 3 lists the contributors to this study; their cooperation is gratefully acknowledged.

2. Governmental user survey - Several United States and foreign government agencies were contacted in the effort to obtain safety and performance data generated by the use of lithium batteries in actual military and space applications. Table 4 lists these contributors; their contributions are gratefully acknowledged.

3. Information retrieval sources - A significant number of documents relating to the safety studies and performance characteristics for many of the major lithium primary battery systems are listed in various governmental and private database systems. The databases employed for the present study and the search period covered are given below:

   - o CA SEARCH, Chemical Abstracts, American Chemical Society (1967 to 12 October, 1984).

   - o NTIS, National Technical Information Service, U.S. Dept. Commerce (1964 to 1984).

   - o DOE ENERGY, Department of Energy (1974 to August, 1984).

   - o ELECTRIC POWER DATABASE, Electric Power Research Institute (1972 to October 1984).

   - o ENERGYLINE, Environmental Information Center, Inc. (1970 to October, 1984).

   - o Ei ENGINEERING MEETINGS, Engineering Information, Inc. (1980 to September, 1984).

   - o SCISEARCH, Institute for Scientific Information (1974 to 13 December 1984).

TABLE 3. STUDY CONTRIBUTORS FROM THE LITHIUM BATTERY MANUFACTURING, USER, OR DISPOSAL SECTORS

Contributor(s)	Company	Location	Li System(s)/Studies
N. Beebe	Battery Disposal Technology, Inc.	Clarence, NY	Disposal
J.D. Jolson F.R. DiPietro	Catalyst Research Corp.	Owings Mills, MD	I_2 FeS_2 (Thermal)
D. Linden	Duracell Inc.	Bethel, CT	SO_2 MnO_2
R.A. Brown	Eagle-Picher	Joplin, MO	$SOCl_2$ $(CF_x)_n$
D.J. Trevoy	Eastman Kodak	Rochester, NY	$(CF_x)_n$
K.M. Abraham	EIC Laboratories	Norwood, MA	SO_2 $SOCl_2$ TiS_2 V_6O_{13} $Cr_{0.5}V_{0.5}S_2$
P.W. Krehl	Electrochem Industries	Clarence, NY	BrCl in $SOCl_2$ Cl_2 in SO_2Cl_2 $AgVO_x$
R.G. Zalosh	Factory Mutual Research Corp.	Norwood, MA	SO_2 Disposal
P.C. Congleton	Gould Defense Systems	Cleveland, OH	H_2O H_2O_2
E.L. Littauer	Lockheed Missiles & Space	Palo Alto, CA	Ag_2O_2 O_2
G.H. Boyle F.W. Dampier A.J. Miserendino	GTE	Waltham, MA	$SOCl_2$
N. Marincic	Hellesens Battery Engineering	Hyde Park, MA	$SOCl_2$

TABLE 3. (Cont.)

Contributors	Company	Location	Li System(s)/Studies
H.V. Venkatesetty	Honeywell	Bloomington, MN	SO_2 V_2O_5
D.L. Chua	Honeywell	Horsham, PA	SO_2 $SOCl_2$
J.A. Stiles	Moli Energy Ltd	Burnaby, B.C. Canada	MoS_2
R. Morioka K. Tsubaki	Panasonic Industrial Co.	Secaucus, NJ Arlington Hts., IL	$(CF_x)_n$
S. Chodosch M.R. Lembo J.R. Sullivan	Power Conversion Inc.	Elmwood Park, NJ	SO_2 $SOCl_2$
M.J. Brookman K.K. Press	SAFT America	Cockeysville, MD	$SOCl_2$ MnO_2 CuO $Cu_4O(PO_4)_2$
A. Sprinzak D. Yehiely	Tadiran	Rehovot, Israel	SO_2 $SOCl_2$
G.E. Blomgren C.M. Langkau	Union Carbide Corp.	Westlake, OH	$SOCl_2$ MnO_2 FeS_2

TABLE 4. STUDY CONTRIBUTORS FROM VARIOUS GOVERNMENTAL AGENCIES

Contributor(s)	Governmental Agency	Location	Li System(s)/Studies
G.J. Donaldson	Defence Research Establishment Ottawa	Ottawa, Ontario, Can.	SO_2 MoS_2
G.J. DiMasi E.H. Reiss, Jr.	ERADCOM, U.S. Army	Ft. Monmouth, NJ	SO_2
J. Bene	NASA Langley	Hampton, VA	SO_2
B.J. Bragg	NASA Johnson	Houston, TX	BrCl in $SOCl_2$
H. Frank G. Halpert	NASA Jet Propulsion Laboratory	Pasadena, CA	$SOCl_2$
J.A. Barnes R.F. Bis S.D. James W.P. Kilroy D. Warburton W.V. Zajac, Jr.	NSWC, U.S. Navy	White Oak, Silver Spring, MD	SO_2 $SOCl_2$ BrCl in $SOCl_2$ Cl_2 in SO_2Cl_2 $(CF_x)_n$
S. Shuler S.P. Wharton	NWSC, U.S. Navy	Crane, IN	Several Systems
S.C. Levy	Sandia National Laboratories	Albuquerque, NM	SO_2, glass seals
R.A. Marsh	Wright Patterson Aero Propulsion Laboratory	Wright Patterson AFB, OH	$SOCl_2$

- CONFERENCE PAPERS INDEX, Cambridge Scientific Abstracts (1973 to September, 1984).

- SSIE CURRENT RESEARCH, National Technical Information Service, U.S. Dept. Commerce (1978 to mid-1982).

4. Open technical literature.

5. Independent test facility reports - Many lithium battery manufacturers and several governmental agencies submitted Underwriter Laboratory, Inc. reports for specific cell sizes. These cells have completed testing in the UL Component Recognition Program. Table 5 summarizes the testing program conducted at UL.

For the convenience of the reader, references for all chapters appear at the end of the chapter.

TABLE 5. TEST CONDITIONS FOR LITHIUM CELLS SUBMITTED TO UNDERWRITERS LABORATORIES INC. FOR COMPONENT RECOGNITION

Test	Test Conditions	Number of Cells	Test Parameters
1. Oven Exposure	Fresh cells stored at 71°C for 90 days	40	Cell OCV and Weight before and after test
2. Temperature Cycling	Ten sequences of: 16h at -54°C, 8h at ambient temperature, and 16h at +71°C.	20	Cell OCV and Weight before and after test
3. Partial Discharge	a) Discharge to 1/3 capacity at 25°C	20	All cells to be used in subsequent test procedures. Rates are not specified for cells discharged at 25°C. Discharge rates for cells stored at 71°C are, approximately, C/2200 and C/4300 to the 1/3 and 2/3 capacity levels, respectively.
	b) Discharge to 2/3 capacity at 25°C	20	
	c) Discharge to 1/3 capacity at 71°C during 60 days	35	
	d) Discharge to 2/3 capacity at 71°C during 60 days	35	
4. Short Circuit	Cell terminals connected to provide a short circuit condition at 25 and 60°C (½ number of cells at each temperature):		Monitoring of cell case temperature and observation for indications of reaction. Resistance value of the short circuit is not given
	Fresh cells	10	
	After test 1	10	
	After test 2	10	
	After test 3a	10	
	After test 3b	10	
	After test 3c	10	
	After test 3d	10	

TABLE 5. (Cont.)

Test	Test Conditions	Number of Cells	Test Parameters
5. Heating	Cells heated by an external source to a temperature of 180°C, maximum:		Monitoring of cell case temperature and observation for indications of reaction
	Fresh cells	5	
	After test 1	5	
	After test 2	5	
	After test 3a	5	
	After test 3b	5	
	After test 3c	5	
	After test 3d	5	
6. Crushing	Cells crushed in a vise:		Monitoring of cell case temperature and observation for indications of reaction
	Fresh cells	5	
	After test 1	5	
	After test 3c	5	
	After test 3d	5	
7. Humidity	Cells subjected to the sequences of the conditions of Method 507.1 of MIL-STD-810C at temperatures to 65°C and relative humidities to 90-100% for 6h followed by temperature reduction to 30°C in 16h (minimum relative humidity 85%):		
	Fresh cells	5	
	After test 1	5	
	After test 3c	5	
	After test 3d	5	
8. Vibration	Cells subjected to Vibration Test I, MIL-B-18D, simple harmonic motion of 0.06 in (0.15 cm) total maximum excursion. Frequency varied at rate of one Hz per minute between 10 and 55 Hz and return in not less than 90 minutes or more than 100 minutes. Tests conducted in three mutually perpendicular directions:		
	Fresh cells	5	

TABLE 5. (Cont.)

Test	Test Conditions	Number of Cells	Test Parameters
8. (Cont.)	After test 1	5	
	After test 3c	5	
	After test 3d	5	
9. Drop	Cells from test 8 dropped from a height of six feet (1.83 meters) onto a concrete floor.		
10. Forced Discharge and Recharge	Cells forced discharged and then subjected to a charging current:		Monitoring of cell case temperature and observation for indications of reaction Current values are not given
	Fresh cells	10	
	After test 1	5	
	After test 2	5	
	After test 3a	5	
	After test 3b	5	
	After test 3c	5	
	After test 3d	5	
	Totally discharged	10	

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CHAPTER 2

SAFETY DESIGNS FOR LITHIUM BATTERY APPLICATIONS

The safety and hazard characteristics for lithium electrochemical cells and batteries have been of major concern to both the user and manufacturing communities since the early 1970's. Intensive research and development efforts since that time focused upon alleviating or eliminating the hazards associated with thermal abuse and such electrical abuse conditions as short circuit, forced overdischarge, and charge. This chapter briefly discusses some of the safety-related measures lithium cell manufacturers, private industry, and the U.S. military have developed for cells and batteries of the major lithium primary electrochemical systems, $Li-(CF_x)_n$, $Li-MnO_2$, $Li-SO_2$, and $Li-SOCl_2$.

LITHIUM CELLS

Improvements in the safety characteristics at the cell level are the result of the use of improved separators, chemical additives, vent mechanisms, glass-to-metal or ceramic-to-metal hermetic seals, electrolytes with reduced water content, coulombically balanced stoichiometries, and internal electric and thermal fuses. Specific examples are given for each of the above primary lithium electrochemical systems:

1. Lithium-polycarbon monofluoride, $Li-(CF_x)_n$

Panasonic (Matsushita) $Li-(CF_x)_n$ cells possess a crimped plastic cover composed of a low melting thermoplastic resin.[1] As cell temperatures increase as a result of thermal abuse or self-heating due to high discharge rates, the plastic cover deforms sufficiently to allow the escape of electrolyte. When the Panasonic BR-2/3A cell was considered as the power supply for the Kodak Disc Camera, cells developed internal short circuits following drop tests.[2] Ventings occurred under these conditions and after external short circuit tests. A joint program between Panasonic and Kodak resulted in the development of a modified

polypropylene separator designed to inhibit ion flow in cells discharged at high rates or subjected to short circuit conditions. In addition, Kodak Disc Camera batteries, comprised of two BR-2/3A cells in series, are electrically connected by a thermal fuse. It is important to note that no safety-related incidents have been reported for this consumer battery.[3]

2. Lithium-Manganese dioxide, Li-MnO_2

The major safety features of Li-MnO_2 cells is the incorporation of various types of vent structures designed to relieve the high internal pressures resulting from exposure to elevated temperatures or prolonged high rate discharge:[4]

- o Sanyo and General Electric - resealable vents in the anode caps of button cells or cell tops of cylindrical cells.
- o Duracell - coined or stamped weakened areas in case bottoms.
- o Panasonic (Matsushita) - cell covers of a low melting thermoplastic resin which weaken at elevated temperatures.
- o Varta - some cylindrical cells and batteries possess puncturable diaphragms in the case top.

3. Lithium sulfur dioxide, Li-SO_2

The most intense efforts (and the most successful) relative to the development of relatively safe, stoichiometrically balanced Li-SO_2 cells and batteries were the result of cooperative research and development programs between the personnel at LABCOM (formerly ERADCOM) and the technical personnel at Duracell, Inc. and Power Conversion, Inc. Cells and batteries procured under MIL-B-49430(ER) and its Amendments[5] possess the following safety features:

A. <u>Cells</u>

- o Hermetic seals comprised of special non-corroding glasses such as the Sandia TA-23 glass.[6]
- o Reliable mechanical vent structures designed to open at internal pressures of about 30 atmospheres (3040 kPa). This pressure corresponds to approximate cell temperatures of 105 to 115°C, a value well below the melting point of lithium metal (180.5°C).
- o Water levels less than 1000 ppm.
- o Coulombically balanced Li to SO_2 ratio.

B. Batteries

- o Nonreplaceable time delay fuse(s) at minimum current ratings.
- o Thermal fuse(s) or thermal cutoff device(s) are designed to interrupt the circuit at temperatures of 190±5°F (88±3°C). The location of each thermal fuse is specified.
- o Diode protection against inadvertent electrical charging form an external source or from one string of cells to a weaker cell or string of cells (e.g., BA-5598 or BA-5513).
- o All intercell connections and battery leads to the connector are insulated.
- o Connector is recessed.

In addition to the above, the U.S. Army (LABCOM) conducts an analysis of two percent of all batteries and routinely subjects additional batteries to an abuse testing program for quality control purposes. Table 6 shows the nine $Li\text{-}SO_2$ batteries currently purchased under MIL-B-49430(ER) and its Amendments. It is important to note that eight safety incidents have occurred for batteries procured under MIL-B-49430 (i.e., since 11 December 1981).[7]

4. Lithium-thionyl chloride, $Li\text{-}SOCl_2$

Lithium-thionyl chloride are produced in a variety of designs (e.g., spirally wound, prismatic, and bobbin internal structures). Cells and batteries do incorporate electrical and thermal fusing, where required, but, in general, lack a reliable low pressure mechanical vent which is designed to open at internal cell temperatures between 90°C and 120°C. Instead, many manufacturers rely on the cracking of the glass-to-metal or ceramic-to-metal seals as the venting mechanism for cells subjected to extreme abusive conditions. Research and development efforts have been concerned with developing methods to drastically limit the possibility for hazardous reactions by using electrode limited electrochemical designs, including electrical and thermal safety devices within the cell structure, restricting the electrode surface area (e.g., bobbin designs, disc cells), and by incorporating chemical additives such as BrCl as a cosolvent with $SOCl_2$ (increased solubility of S in $SOCl_2$),[3] copper or copper salts in the carbon electrode[9,10] (ohmic bridging between electrodes subjected to forced overdischarge conditions), and poisoning agents[11,12] to deactivate the cell at elevated temperatures.

TABLE 6. ELECTRICAL AND THERMAL PROTECTIVE DESIGN FEATURES FOR U.S. ARMY LITHIUM-SULFUR DIOXIDE BATTERIES (MIL-B-49430(ER))

U.S. Army Battery Designation, BA-XXXX/U	Maximum Open Circuit Voltage, V	Number of cells	Battery Electrical Design	Electrical Fuse(s), A	Blocking Diode(s)	Thermal Fuse(s)
5567	3.05	1	Single cell	none	none	none
5847	6.10	2	Series	2.25	1	1
5599	9.15	3	Series	2.25	1	1
5600	9.15	3	Series	2.25	1	1
5588	15.25	5	Series	1.0	1	1
5598	3.05/15.25 (A1/A2)	5	Series, 2 Sections	2.25 (two)	2	2
5513	15.25	10	2 parallel strings of 5 cells in series	2.25	2	2
5557	30.50	10	2 series connected sections of 5 cells in series	0.8 (two)	2	2
5590	30.50	10	Same as 5557	2.25 (two)	2	2

NOTES: 1. The 2.25A electrical fuse in the BA-5600/U battery is located in the positive lead. The 2.25A electrical fuses for the BA-5598/U battery are located in the (-A1, -A2) and +A1 leads. All other batteries possess fuses in the negative leads. The specification required electrical fuses to be nonreplaceable and to react on a time delay basis.

2. Blocking diode characteristics (Section 3.5.5.2, Amendment 3, MIL-B-49430(ER)): Forward current, I_F = 3A
Forward voltage drop, V_F = 0.55 $\pm$ 0.1V
Reverse current, I_R = 2mA
Reverse voltage, V_R = 40V

3. Thermal switch (thermal fuse) characteristics (Section 3.5.5, MIL-B-49430(ER)): Switch remains closed at 180°F (82°C) and below.
Switch opens at 190$\pm$5°F (88$\pm$3°C).

After an extensive design review process, end items containing batteries are submitted to the U.S. Navy for testing in accordance with Enclosure 2 of NAVSEANOTE 9310. Figure 1 shows the most common battery design circuits employed for Navy applications.[13] It is important to note that, for batteries comprised of more than one cell, the electrical and thermal fuses are located in the negative (ground) leg of the battery. Should the fusing be placed in the positive lead, any short circuit between the cell case and a grounded end item structure would bypass the protective electrical fuse. Many manufacturers will include miniature fuses or fuse links within the void space between the cell lid and the false cap. This additional safety precaution further restricts the possibility for hazards to occur when intercell short circuits develop. Diodes are to be installed in each series string of cells when batteries consist of two or more strings electrically connected in parallel.

Figure 2 shows the circuits for cells (or batteries) which act as support power supplies to a mains (DC) power supply.[14] Lithium electrochemical cells or batteries will explode or vent violently when subjected to high current levels. Thus, it is important that extreme caution be taken in designing protective circuiting in these applications.

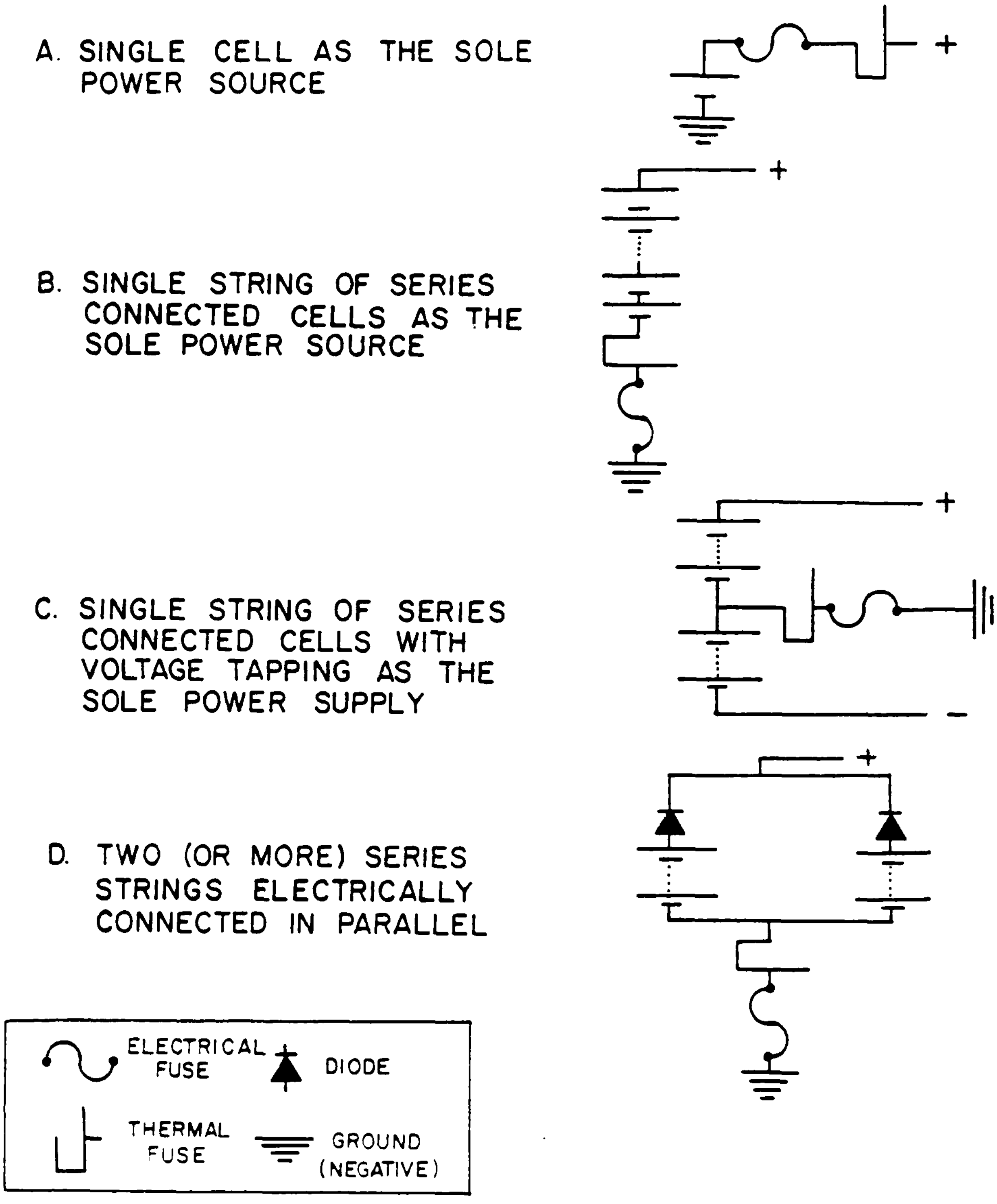

FIGURE 1. U.S. NAVY ELECTRICAL CIRCUIT DESIGN RECOMMENDATIONS

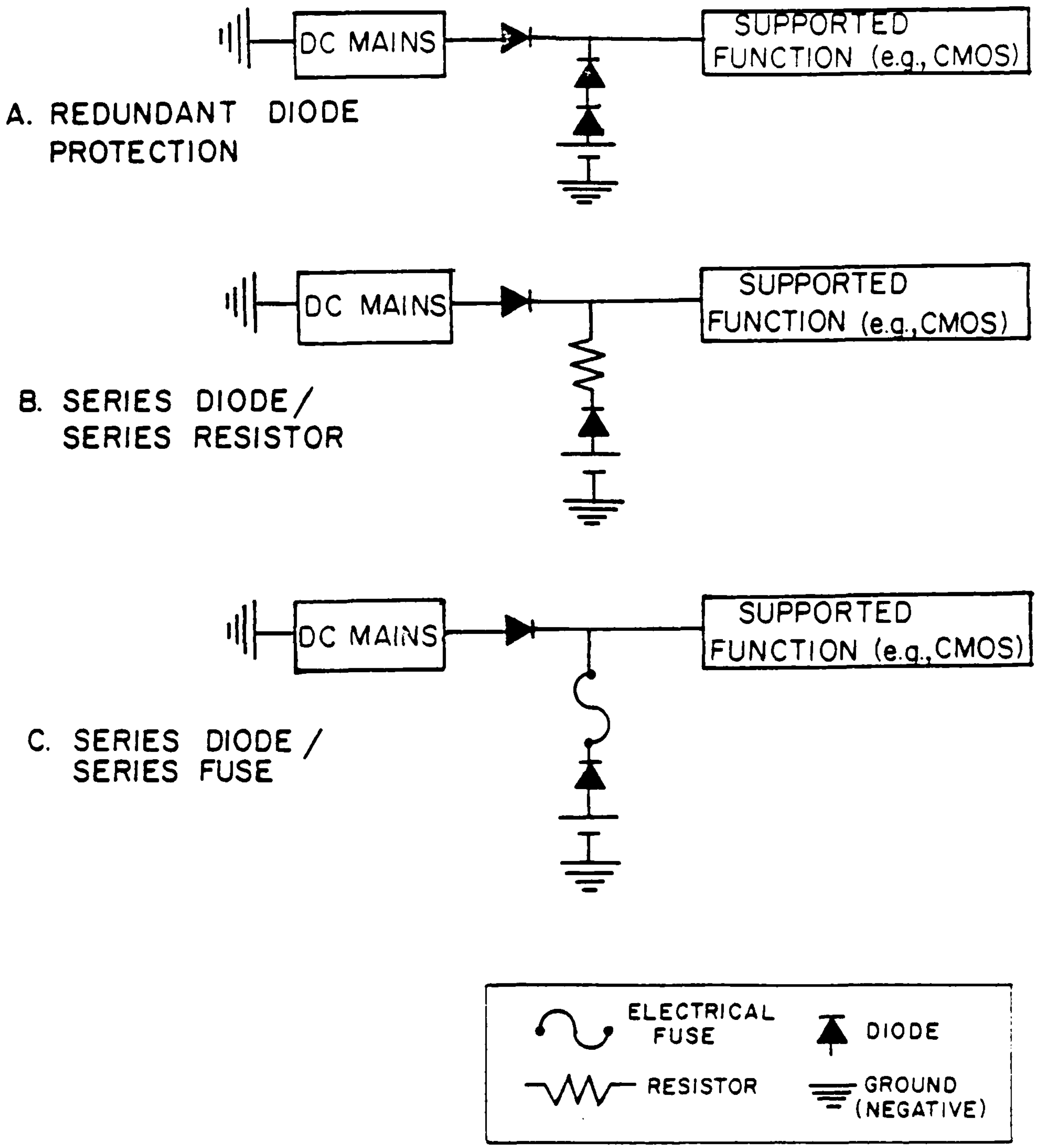

FIGURE 2. PROTECTIVE CIRCUITS FOR CELLS (OR BATTERIES) USED AS SUPPORT POWER SUPPLY TO A MAINS (DC) POWER SUPPLY

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CHAPTER 3

TRANSPORTATION, STORAGE, AND DISPOSAL

INTRODUCTION

Thus far, the major emphasis of this work has been concerned with the safety characteristics for lithium cells and batteries subjected to electrical, thermal, and mechanical abuse conditions. The results of such data constitute the primary basis in determining which specific cell systems and/or cell sizes should be exempt from testing in accordance with procedures in NAVSEANOTE 9310. However, it has become increasingly apparent that other factors such as the safe transportation, storage, and disposal of lithium cells and batteries should be of equal importance.

The first descriptions relative to the possible hazards associated with lithium cell and battery transportation, storage, or disposal were voiced by Brooks[1] of the U.S. Army Electronics Technology and Devices Laboratory (ECOM, presently LABCOM) and Warburton[2] of the Naval Ordnance Laboratory, White Oak (presently the Naval Surface Weapons Center [NSWC]) in 1974. In subsequent studies performed by personnel at ECOM and its contractors, these factors in the life cycle of lithium-sulfur dioxide (Li-SO_2) cells and batteries were discussed. Most notable of these studies are the reports by Hunger and Christopulos[3] at ECOM, Watson[4] at Mallory (presently Duracell International), and Glitner[5] at Eagle-Picher. Slimak *et al.*[6] investigated various methods for the environmentally safe disposal of Li-SO_2 cells and batteries. Later, Bowers[7] at NSWC reviewed the safety, storage, and disposal procedures relative to the Li-SO_2 and lithium-inorganic electrolyte cell systems.

In view of the above and in consideration of the possible hazards for lithium cells and batteries when subjected to the various electrical, thermal, and mechanical abuse conditions, a joint subcommittee on lithium battery safety

under the Joint Logistic Chiefs Sub-Panel on Batteries and Fuel Cells was formed in 1977.[7] The subcommittee was comprised of cognizant members of the Army, Navy, and Air Force and later included NASA personnel. This group subsequently became The Lithium Battery Technical/Safety Group. The primary goals of this group are to discuss safety programs, investigate areas of common interest, give guidance to lithium cell and battery users within the U.S. military and NASA, and to exchange pertinent information relative to the safe use, deployment, and disposal of lithium cells and batteries.[7,8] It is important to note that the procurement, use, storage, and disposal practices differ markedly within each U.S. military organization and NASA. Consequently, each department has developed its own policies. The U.S. Army purchases Li-SO_2 cells and batteries in accordance with MIL-B-49430 (ER), its amendments,[9] and the terms of the procurement contract. The policies governing the handling, use, and disposal of U.S. Army cells and batteries have been discussed by Reiss[8] and more recently, by Berger.[10,11] The U.S. Navy, in turn, procures the end use item from the prime contractor and performs extensive safety design reviews, analyses, and tests upon candidate lithium power supplies. Bis and Barnes[12] discussed the U.S. Navy policies governing the deployment and implementation of lithium batteries. Presently, these guidelines are specified in NAVSEANOTE 9310.[13]

TRANSPORTATION

The United States Department of Transportation (DOT) regulates the commercial shipment of hazardous materials within the United States, the District of Columbia, the Commonwealth of Puerto Rico, the Territory of Guam, and the Possessions of American Samoa and the Virgin Islands. Prior to 1974, lithium cells and batteries were not officially recognized as hazardous materials and, as a result, were not regulated by any existing clauses in Title 49, Code of Federal Regulations, Transportation (49 CFR).[14] By 1974, investigations had been initiated to determine the causes of several safety related incidents involving lithium-sulfur dioxide cells and batteries experienced by the military and the commercial airline industry.[7] In response to the growing numbers of these safety-related incidents and their implication to the safe transport of lithium cells and batteries in commerce, the DOT temporarily prohibited shipment of these items.[8] After an exhaustive review procedure, lithium cell and battery policies

were then formulated and incorporated into 49 CFR. The DOT subsequently granted Power Conversion Incorporated (PCI) Special Permit 7052 on September 23, 1975.[8] Since that time, Special Permit 7052 was changed to Exemption DOT-E 7052 which is presently in its fifteenth revision.

The Federal Aviation Administration (FAA) investigated several safety related incidents on board commercial and private aircraft. These accidents were specifically concerned with the use of lithium-sulfur dioxide batteries in such emergency equipment as Emergency Locator Transmitters (ELTs), the slide rafts, auxiliary lighting, and portable announcement devices. On December 4, 1975, the FAA issued a report[7] recommending that the lithium-sulfur dioxide batteries be comprised of hermetically sealed cells which incorporate a safety vent mechanism. It was further recommended that electrical fuses be employed in series-connected strings of cells. However, instances of explosions, violent ventings, and gas leakage from these batteries continued to occur. By 1979, a total of 562 accidents or other safety related incidents were reportedly[15] documented by the FAA. As a result, the FAA issued an Airworthiness Directive (AD) in February, 1979 which imposed a ban on the use of lithium-sulfur dioxide batteries on passenger-carrying aircraft. A second AD published in the Federal Register on August 27, 1979 required that all lithium-sulfur dioxide batteries to be installed in passenger-carrying aircraft must meet the requirements prescribed in Technical Standard Order (TSO)-C97 of the same date.[8,15] This TSO specifies the environmental tests of salt water immersion, shock, vibration, high temperature storage, temperature cycling, and altitude testing. The required electrical abuse tests include short circuit, charge, and forced discharge. In order to comply with the AD, candidate batteries must exhibit no evidence of leakage, loss of capacity, venting, physical damage, or malfunction of the safety mechanisms during any of the environmental or electrical abuse tests in TSO-C97. Proof of a reliable vent mechanism and cell hermeticity is also required. Mallory (Duracell International) qualified two lithium-sulfur dioxide batteries, each comprised of three LO-26S cells (D size, no longer manufactured) connected in series.[16] It is believed that, at present, no domestic, passenger-carrying commercial aircraft utilizes lithium-sulfur dioxide batteries in emergency equipment due, in part, to the high costs involved in the required requalification testing for each change in cell or battery design.

Lithium cells, batteries, and electronic components or end items containing lithium cells or batteries are considered as hazardous materials for purposes of shipment and are regulated in the United States by the DOT in accordance with 49 CFR. Presently, there exist three general classifications for the transportation of newly fabricated, undischarged lithium cells and batteries:

1. 49 CFR 173.206f states that lithium batteries of one or more cells be exempt from the requirements of Subchapter C - Hazardous Materials Regulations provided that a) "each cell contain no more than 0.5 gram of lithium or lithium alloy, b) each battery may contain an aggregate quantity of no more than 1 gram of lithium or lithium alloy, c) each cell must be hermetically sealed, d) cells must be separated so as to prevent short circuits, e) batteries must be packed in strong outside packaging except when installed in electronic devices, and f) if a battery contains more than 0.5 gram of lithium or lithium alloy, it may not contain a liquid or gas that is a hazardous material according to this subchapter unless the liquid or gas, if free, would be completely absorbed or neutralized by other materials in the battery."

2. Exemption DOT-E 7052 (Fifteenth Revision) authorizes the commercial transportation by motor vehicle, rail freight, cargo vessel and cargo-only aircraft of primary lithium cells and batteries containing the specific cathode materials of vanadium pentoxide (V_2O_5), manganese dioxide (MnO_2), sulfur dioxide (SO_2), polycarbonmonofluoride or monofluorographite ($(CF_x)_n$, where x is approximately 1), thionyl chloride ($SOCl_2$), and sulfuryl chloride (SO_2Cl_2). Also included in this exemption are the secondary lithium cells and batteries containing the cathode materials of titanium disulfide (TiS_2) and molybdenum disulfide (MoS_2), listed as "lithium molybdenum disulfide."

   Lithium cells which have been discharged to the extent that the open circuit voltage (OCV) is less than 2V or batteries containing such cells are not authorized for shipment under DOT-E 7052. It is important to note that cells of the secondary cell system, Li-MoS_2, are shipped in a more stable, semi-charged state.[17] The corresponding OCV of each cell is about 1.8V.

The salient features of this exemption are given below:

a) Proper shipping name: Lithium Batteries.

b) Packaging requirements include:

- o limitations of the maximum amount of lithium to 12g per cell (46 Ah, maximum capacity) and a maximum amount of 500g of lithium in one strong fiberboard container. Separation of inner containers and all inner surfaces by at least one inch thickness of vermiculite or equivalent material is required for the shipment of lithium cells and batteries in drums.
- o package labeling: FLAMMABLE SOLID.
- o an effective means to prevent external short circuits for each cell and battery.
- o the incorporation of a safety venting device in each cell or battery or possess a design which will preclude violent rupture under any conditions incident to transportation (e.g., "dead short").
- o the inclusion of appropriately positioned diodes in those batteries containing cells or series strings of cells electrically connected in parallel.
- o short circuit testing of three representative cells from each week's production of a specific cell type and one representative battery from each week's production of a given battery type in accordance with the procedures prescribed by Abens[18] in Appendix B (sections 3.2.1(1) and 3.2.2(1), respectively) of ECOM Report 73-0242-F.
- o testing of a minimum of ten cells and one battery of each type of each week's production by exposure to an environment of 75°C for 48 hours. No evidence of leakage, distortion, or internal heating must be exhibited.

c) Special provisions of this exemption include:

- o the capability to reship cells and batteries covered by DOT-E 7052 in any of the authorized packages provided the regulations in 49 CFR 173.22a are met.
- o the requirement that a copy of DOT-E 7052 be carried aboard each vessel and aircraft transporting packages covered by the exemption.

- The requirement that the outside container for shipment by cargo-only aircraft be a removable head drum of DOT specification 17H or 17C series or equivalent which is equipped with a gastight gasket. The required outside container for shipment by motor vehicle, rail freight, or cargo vessel must be either a strong wooden box, DOT specification 12B fiberboard box, a DOT specification 21C fiber drum, or a DOT specification 17H or 17C metal drum as authorized for cargo-only aircraft.
- Hermetically sealed cells containing no more than 12g of lithium having V_2O_5, $(CF_x)_n$, MnO_2, $SOCl_2$, SO_2, $SOCl_2$/bromine complex (i.e., BrCl in $SOCl_2$), SO_2Cl_2 and chlorine (i.e., Cl_2 in SO_2Cl_2), TiS_2, and MoS_2 (i.e., lithium molybdenum disulfide) as cathode materials and batteries constructed from such cells are exempt from the requirements for short circuit testing, the <u>weekly</u> thermal stability testing, and the DOT specification 17H or 17C removable head drum for shipment by cargo-only aircraft. However, prior to the first shipment, 10 cells or four batteries of each type to be offered for transportation must pass a series of tests without exhibiting any evidence of leakage, out-gassing, loss of weight, or distortion. These tests are:
  1) A six hour storage of the cells or batteries at a pressure corresponding to an altitude of 50,000 feet (1.7 psi, 11.7 k Pa) at 24 $\pm$ 4°C.
  2) Following the above test, the cells or batteries are required to be subjected to the previously described thermal stability test (storage at 75°C for 48 hours).
  3) The cells or batteries shall be subjected to the vibration test regime given in paragraph 8e iii of DOT-E 7052.
  4) Batteries shall also be subjected to the shock test regime given in paragraph 8e iv of DOT-E 7052.

d) Packages of lithium-manganese dioxide batteries do not require the FLAMMABLE SOLID label for transport in a motor vehicle

provided: 1) the batteries be comprised of no more than four cells which meet the maximum lithium weight and specifications of 49 CFR 173.206f (Half Gram Rule), and 2) the gross weight of a package or packages in one motor vehicle does not exceed 65 pounds (29.5 kg).

It is interesting to note that no exemptions are currently in effect for cells and batteries containing lithium metal in excess of that specified by 49 CFR 173.206f and containing the cathode materials of iodine (I_2), copper (II) oxide (CuO), copper (II) oxyphosphate ($Cu_4O(PO_4)_2$), copper (II) sulfide (CuS), iron (II) sulfide (FeS), and iron (IV) sulfide (FeS_2).[19] Ray-O-Vac Corporation at one time held exemption DOT-E 8349 for the transport of a Li-CuS four cell "9 V" battery (NEDA L 1604). The exemption was not renewed after December 1, 1983 and the battery is no longer commercially available.[20] In addition to the above, the Department of Transportation has not issued any <u>de minimis non curat lex</u> rulings for any lithium cell or battery.[19] Such a ruling would imply that the degree of risk for a safety related incident in the transportation of such lithium cells and batteries would not be worth consideration.

3. Special DOT exemptions have been issued for lithium cells containing amounts of lithium metal in excess of the 12g limitation specified in DOT-E 7052, for lithium-thionyl chloride reserve batteries, and for the transport of lithium cells and batteries in passenger-carrying aircraft. Each of the three classes of special exemptions are discussed below:

   a) Exemptions DOT-E 8141 and DOT-E 8979 were granted to GTE Products Corporation and A/S Hellesens, respectively, for the transportation of lithium-thionyl chloride cells and batteries containing more than 12g per cell. Features of both exemptions are summarized below:

	DOT-E 8141	DOT-E 8979
Proper shipping name	Lithium batteries	Lithium batteries
Li metal weight limit per cell	---	50g (193 Ah)

	DOT-E 8141	DOT-E 8979
Capacity limit per cell	10,000 Ah (2.6 kg Li)	---
Capacity limit per module	30,000 Ah	---
Discharge rate capability	---	"low"
OCV limit for any cell	---	not less than 2V
Packaging	1) Outside packaging of wooden boxes. 2) Inside packaging per application. 3) Single cell packaging per 49 CFR 173.206.	1) Outside packaging of a non-DOT open head, steel drum per application. 2) Cell and battery packaging of 3 mil polyethylene bags. 3) Cushioning of mineral wool, vermiculite or equivalent.
Required labeling	FLAMMABLE SOLID and DANGEROUS WHEN WET	FLAMMABLE SOLID
Authorized modes of transportation	Motor vehicle Cargo vessel	Motor vehicle Cargo vessel Rail freight Cargo-only aircraft
Specific electrical safety requirements	---	1) Each cell and battery must be equipped with effective means to prevent external short circuits. 2) Each cell and battery must incorporate a safety venting device to preclude a violent rupture under any conditions incident to transportation. 3) Batteries containing cells or series of cells connected in

	DOT-E 8141	DOT-E 8979
Specific electrical safety requirements (cont.)		parallel must be equipped with diodes to prevent reverse current flow (charging).
Safety control measures	Labels and packaging required (see above).	1) Label and packaging required (see above). 2) Weekly short circuit and thermal stability testing of cells and batteries as in DOT-E 7052 discussion is required.
Special provisions	1) Batteries must be constructed per manufacturers' specifications. 2) Vans used to transport batteries must be subcontracted from an experienced hazard material transporter. Packages must be blocked and braced. 3) Exemption copy must accompany shipment. 4) Drivers must be cognizant of safeguards and procedures. 5) Packages shipped by cargo vessel must be stowed on deck and protected from the weather. 6) Packages received by persons may be reshipped provided the regulations of 49 CFR 173.22a are met.	1) Cells authorized under this exemption are exempt from the requirements given in section 2 of the safety control measures (above) provided that compliance with the altitude, thermal stability, vibration, and shock (batteries) tests given in the DOT-E 7052 discussion is met. Tests must be conducted prior to the first shipment. 2) Exemption copy must accompany shipment aboard each cargo vessel and aircraft. 3) Packages received by persons may be reshipped provided the regulations of 49 CFR 173.22a are met.

b) Exemptions DOT-E 8564 and DOT-E 9181 were granted to the Altus Corporation and Honeywell Incorporated, respectively, for the transportation of lithium-thionyl chloride reserve batteries. The Altus exemption relates to the power supply for the Expendable Reliable Acoustic Path Sonobuoy (ERAPS). The salient features of each exemption are given below:

	DOT-E 8564	DOT-E 9181
Proper shipping name	Lithium metal and thionyl chloride solution.	Lithium metal and thionyl chloride solution.
Packaging and safety control measures	1) DOT 19A wooden box with cushioning to prevent unnecessary movement.	1) Non-DOT stainless steel vessel per application. 2) Above unit must be placed in a strong wooden box. 3) Electrical leads of actuator mechanism must be shorted. 4) Not more than two pounds of Li metal and not more than 33 pounds of $SOCl_2$ solution in one inside package.
Authorized modes of transportation	Motor vehicle Cargo vessel	Motor vehicle
Special provisions	1) Battery construction must be as shown on specific ERAPS drawings. 2) Packages received by persons may be reshipped provided the regulations of 49 CFR 173.22a are met. 3) Exemption copy must accompany shipment. 4) Drivers of motor vehicles and masters of vehicles must be	1) Packages received by persons may be reshipped provided the regulations of 49 CFR 173.22a are met.

	DOT-E 8564	DOT-E 9181
Special provisions (cont.)	instructed in safeguards and procedures.	

c) Three exemptions have been granted which authorize the commercial transportation of a single lithium cell (Texas Instruments Incorporated) or multiple lithium cells and batteries (Duracell Incorporated and Eastman Kodak Company) aboard passenger-carrying aircraft. The features for each exemption are summarized below:

	DOT-E 8457	DOT-E 9348	DOT-E 9355
Exemption holder (cell system)	Texas Instruments (Duracell Li-SO_2 cell)	Duracell (Li-MnO_2)	Kodak (Li-MnO_2 and Li-$(CF_x)_n$)
Proper shipping name	Flammable solid n.o.s. (not otherwise specified)	None	None
Labeling required	"FLAMMABLE SOLID, N.O.S." and "DOT-E 8457"	None	None
Packaging and safety control measures	1) Packaging as described in application	1) Batteries in devices or in packaging supplied by manufacturer. 2) Batteries must be Li-MnO_2 and may not contain more than 2g Li. No component cell of the battery may contain more than 0.5g of lithium. 3) No more than six batteries may be carried by a passenger or crew member on their person, carry-on luggage, or checked baggage.	1) Packaging are fiberboard, wood, or plastic boxes in compliance with appropriate paragraphs of 49 CFR 173.24 except that batteries in electronic devices need not be packaged. 2) Batteries must be separated to prevent short circuits. 3) Batteries must be of the Li-MnO_2 or or Li-$(CF_x)_n$ and may not contain more than 2g lithium. No component cell of any battery may contain more than 1.5g of lithium.

	DOT-E 8457	DOT-E 9348	DOT-E 9355
Authorized modes of transportation	Motor vehicle Rail freight Cargo vessel Cargo-only aircraft Passenger-carrying aircraft but no no package may be carried in the passenger compartment of an aircraft.	Passenger carrying aircraft	Motor vehicle Rail freight Cargo vessel Cargo-only aircraft Passenger-carrying aircraft
Special provisions	1) Prior to first shipment of lithium cells in electronic devices, shipper must confirm that the cells comply with all applicable requirements of DOT-E 7052 and FAA TSO-C 97 (see previous discussion). 2) No cell larger than a standard C size may be shipped under this exemption. 3) The maximum current obtainable from any cell shipped may not exceed 30 mA. If necessary, an internal resistor must be used to limit the current. 4) A copy of this exemption must be placed in an envelope and securely attached to the outside of each outside package shipped by air or water. 5) Packages received by persons may be reshipped provided the regulations in 49 CFR 173.22a are met.	1) No requirements of 49 CFR applies to these Li-MnO_2 batteries when offered and transported under the conditions specified in this exemption.	1) Batteries in electronic devices and packages of batteries per this exemption are exempt from 49 CFR Parts 100-199 except as provided: 2) Packages received by persons may be reshipped provided the regulations in 49 CFR 173.22a are met. 3) An exemption copy must be carried aboard each vessel and aircraft used to transport packages covered by the exemption.

At the present time, there is considerable pressure upon DOT to increase the lithium weight limits specified in 49 CFR 173.206f (i.e., the "Half Gram Rule") and to grant exemptions for: a) lithium cells and batteries containing lithium amounts exceeding the limits given in DOT-E 7052, b) lithium cells and batteries of special designs, and c) authorization to transport lithium cells and batteries on board passenger-carrying aircraft. This condition could result in a far too complex set of regulations and exemptions, imposing serious burdens upon both the DOT and the lithium cell manufacturers. In view of the above, a Working Group comprised of interested members of the lithium battery industry, the Department of Defense, the DOT, and the National Electrical Manufacturers Association (NEMA)[21] was formed to develop a NEMA lithium battery standard for transportation. If the group is successful in formulating such a standard or set of standards, elimination of Exemption DOT-E 7052 could occur.[22] In addition, one proposal before the Working Group relates to an increase in lithium weights in the cells and batteries described in 49 CFR 173.206f to 1.0g and 2.0g, respectively. The latter standard would apply only to those cells and batteries which meet the qualification test standards for "2 Gram" batteries and which are packaged per DOT regulations. These NEMA standards would then be referenced by the DOT in accordance with 49 CFR 171.7.

Special transportation regulations exist for spent or otherwise nonfunctional lithium cells and batteries considered to be reactive hazardous wastes. Formerly, exemption DOT-E 8441 only authorized shipment of waste $Li-SO_2$ cells and batteries to a disposal site, provided the cells and batteries met the testing and maximum lithium weight limit of 12g per cell in DOT-E 7052 when newly fabricated. Exemption DOT-E 8441 was incorporated into the regulations as 49 CFR 173.1015 on December 6, 1982. This regulation allows lithium batteries comprised of one or more cells, for disposal, to be offered for transportation to a permitted storage facility and disposal site by motor vehicle only provided all the following conditions are met:

a) When new, the battery contained not more than 12g of lithium per cell.

b) The battery is equipped with an effective means of preventing external short circuits.

c) The battery is classified and offered for transportation as an ORM-C (Other Regulated Material, C signifies that the waste lithium batteries

possesses inherent characteristics which make them unsuitable for shipment unless properly identified and prepared for transportation (49 CFR 173.500)).

d) The battery is overpacked in a strong fiberboard box, or metal or fiber drum in compliance with 49 CFR 173.24.

It is important to note that the above does not apply to lithium batteries which, when new, were excepted from regulation under the Half Gram Rule, 49 CFR 173.206f.

Detailed packaging instructions and specific requirements relative to the safe transport of waste lithium batteries were recently discussed by Wilds.[23] Individual cells can be protected from external short circuits by wrapping each cell in a plastic bag, by taping the terminals or lead wires, or by reusing original packing materials. The outer packaging can be a DOT-specified 12B fiberboard box not to exceed a gross weight of 65 pounds, a DOT-specified 17H or 17C metal drum fitted with a gas tight gasket, or metal drums with removable heads. Individual packages within metal drums must be insulated from each other and the inner drum wall surface by at least one inch of vermiculite or equivalent material such as mineral wool. Only permitted, hazardous waste transport companies may carry lithium batteries for disposal.

The international air transport of commercial lithium cells and batteries by cargo-only aircraft is regulated by either the UN-affiliated International Civil Aviation Organization[24] (UN/ICAO) or the International Air Transport Association[25] (IATA). Both organizations prescribe substantially the same requirements for packaging, testing, and maximum lithium weight limits as for those given in DOT-E 7052 for transport by cargo-only aircraft.[19,26] However, IATA does allow lithium cells and batteries of every solid cathode material to be shipped under its regulations. Thus, cells and batteries comprising the so-called "1.5 V" lithium cell systems and the lithium-iodine cell system may be shipped abroad cargo-only IATA carriers.[25] In addition, IATA utilizes DANGEROUS WHEN WET labels instead of the FLAMMABLE SOLID label requirement of DOT-E 7052. It is important to note that some individual members of IATA have developed specific variations of the Association's regulations.

Exemption DOT-E 7052 is cited as the basic set of regulations for the packaging and transport of lithium cells and batteries in the Departments of the Air Force,[27] Army,[8,28] and Navy[12,13] as well as the National Aeronautics and Space Administration (NASA).[29] Due to the diverse nature of responsibility and activity, each of the above organizations has found it necessary to adopt supplementary policies. The most important features of these policies are given below:

1. The United States Air Force Transportation Regulations administers the transportation of lithium cells and batteries carried by personnel aboard military aircraft. The specific authority to ship lithium cells and batteries during tactical or contingency operations is given in the waiver, AFLC 71-4-85-05.[28] This waiver correlates directly with the Safety Control Measures, Special Provisions, and cargo-only aircraft Requirements of DOT-E 7052 except as regards the following key differences:
   - o Weekly short circuit and thermal stability testing for cells and batteries is not specified in the waiver.
   - o Waiver limits the cathode materials to $(CF_x)_n$, MnO_2, $SOCl_2$, SO_2, BrCl in $SOCl_2$, and Cl_2 in SO_2Cl_2 for the Special Provision tests for altitude, thermal stability, vibration, and shock.

   Spent lithium batteries are prohibited from transport under this waiver.

   Pending changes in Air Force Transportation Regulations will eliminate some packaging restrictions and ease the total ban on the military air transport of used lithium batteries for disposal.[30] It is important to note that these proposed revisions pertain only to U.S. Army procured lithium-sulfur dioxide batteries. Specifically, combat personnel will be allowed to carry equipment containing lithium-sulfur dioxide batteries on board military aircraft during tactical or contingency operations. One or two spare batteries may also be unpacked to aid in rapid deployment. Batteries discharged during combat may be transported by air to the first landing zone with proper packaging facilities.[30] These batteries are then disposed of in accordance with Defense Reutilization Marketing Services instructions. It is believed

that these revisions will receive final approval by the Triservices by July, 1986, with final adoption into the Air Force Transportation Regulations by August/September, 1986.

2. In addition to the transportation-related regulations and policies previously discussed, the United States Army requires that its lithium-sulfur dioxide batteries be packaged in accordance with the Special Packaging Instructions, SPI 1G00066, which have been incorporated into MIL-B-49430(ER).[9]

3. In contrast to the U.S. Army lithium battery procurement policies, the U.S. Navy, in general, purchases the complete end item. As a result, the Navy must extensively review the packaging design to ensure complete safety of the item in transit.[13] For those items which conform to the minimum packaging requirements of DOT-E 7052, complete design disclosures must: a) be obtained prior to limited or full-scale production and b) be incorporated into acquisition specifications, contracts, and manuals. In addition, the packaging must meet the minimum package performance levels as specified in MIL-STD-648. Replacement batteries for the end item are required to be packaged for shipment by cargo-only aircraft. Packaging which does not conform to the minimum specifications of DOT-E 7052 must be reviewed by NAVSEASYSCOM to determine whether the proposed package design is of greater strength and efficiency than DOT-specified containers. A Certificate of Equivalency (COE) will be issued for the proposed container after an extensive review of: a) the results of abuse testing as prescribed in Enclosure 2 of NAVSEANOTE 9310; b) the results for altitude, thermal stability, vibration, and shock testing given in the Special Provisions of DOT-E 7052; and c) the results obtained from environmental tests upon the packaged and unpackaged end item. A complete design disclosure is further required to obtain the COE.

4. NASA does not permit the transport of lithium-sulfur dioxide cells or batteries within the Goddard Space Flight Center unless packaged in accordance with DOT-E 7052.[29] NASA also requires that the Traffic

Management Office of the Logistics Management Division be responsible for the certification of all shipments from Goddard.

STORAGE

Lithium batteries are classified as flammable solids and, as such, are considered to possess the capability to cause fires at any time. Such fires would also pose serious toxicologic hazards through the release of cell contents and the combustion of plastic battery container material, electronic components, and other flammable materials. In view of the above, policies have been developed by the U.S. Army, U.S. Navy, and NASA to regulate the storage of lithium batteries in order to minimize the potential for hazardous conditions.

The U.S. Army policies for lithium-sulfur dioxide battery storage facilities were developed by the U.S. Army Material Dèvelopment and Readiness Command (DARCOM) at the U.S. Army DARCOM Installations and Services Activity, Rock Island, IL.[8,28,31] The source material for the guidelines consisted of the ERADCOM (now LABCOM) Safety Statement for Lithium Batteries, TM 743-200, and National Fire Protection Association (NFPA) Standards 30 and 231.[8] The Army stores lithium-sulfur dioxide batteries at the Sharpe, Red River, and New Cumberland depots. The characteristics for these storage facilities are summarized below:

1. Adequate ventilation is required to prevent the accumulation of SO_2 fumes from leaking cells and batteries. The Threshold Limit Value (TLV) for SO_2 gas has recently been reduced from 5 ppm to 2 ppm.
2. Care must be exercised in moving palletized batteries to prevent mechanical damage by crushing or puncturing.
3. Temperatures in the storage facility should be maintained below 54°C (130°F).
4. The storage facility should preferably be sprinkler-protected if possible. A noncombustible building without sprinklers is considered as the second choice. A combustible building may be used temporarily but other more hazardous commodities must not be stored in the same fire area.[31]
5. The area of piles is limited to 2,000 ft^2 (186 m^2) with a width of no

more than 25 ft (7.6 m). Other dimensional limitations on the storage area include: aisles of 8 ft (2.4 m) or one-half the stack height, a minimum clearance of 2 ft (0.6 m) between a stack and any wall, a minimum clearance of 3 ft (0.9 m) between a stack and any fire door, and at least 3 ft (0.9 m) shall be maintained between the top of the stacks and sprinkler heads. A minimum clearance of 3 ft (0.9 m) shall also be maintained between the top of the stack and the ceiling or roof in a facility without sprinklers.

6. Other materials or commodities will not be stored in the same stack as the batteries.
7. No smoking will be allowed in the battery stack areas.

The U.S. Navy policies for lithium battery storage are given in NAVSEANOTE 9310.[13] These policies require that all lithium batteries and all end items containing lithium batteries which have been approved for use based upon the required testing of NAVSEANOTE 9310 shall be stored in compliance with the requirements given in the end item equipment documents. If such documentation does not exist, new lithium batteries or end items containing lithium batteries, whether ashore or afloat, shall be stored under essentially the same conditions as those required by the U.S. Army. The quantity of stored lithium batteries or end items containing lithium batteries must be kept "to a reasonable minimum". In addition, lithium batteries and end items must be retained in shipping containers to prevent heat transfer between batteries.

Spent lithium batteries or end items with spent lithium batteries which, when new, were approved for fleet use based upon the testing of NAVSEANOTE 9310 must be stored as follows:

1. <u>Ashore</u> - Spent lithium batteries must be sealed in a plastic bag or wrapped in electrically insulated material. These items must be overpacked in a strong fiberboard box, or metal or fiber drum which complies with 49 CFR 173.24. Such packages must be moved to a remote collection point and sprinkler-protected storage area separate from other combustible materials. These stored waste lithium batteries should be disposed of promptly (no more than 30 lbs (13.6 kg) or 30 days). Waste lithium batteries are not to be transported or disposed of

with normally generated refuse. Used lithium batteries shall not be pierced, crushed, burned, dropped, cannibalized, modified, or otherwise carelessly handled; nor can they be electrically abused (short circuited, charged, or reused).

2. Afloat - Spent lithium batteries from ashore deployment or from use while underway are disposed of by discharge overboard in water depths in excess of 100 fathoms (183 m) outside the 50 mile (82 km) limit. These waste lithium batteries shall not be stored for shore disposal.

U.S. Navy policies require different storage conditions for lithium batteries and end items containing lithium batteries which have been approved for use based upon testing other than that prescribed in NAVSEANOTE 9310. These storage requirements are summarized below:

1. Afloat on surface ships - new lithium batteries may be stored on either weather decks or below decks. The quantity of lithium batteries shall be kept at a minimum. Weather deck storage is preferred:
   - o Store batteries in original containers in a drip-proof, self-draining, ventilated metal locker capable of maintaining temperatures below 54°C (130°F).
   - o The storage locker must be isolated from other hazardous and combustible material.
   - o The storage locker must only be used for lithium batteries.

   The requirements for below decks storage are:
   - o Store batteries in original containers in a cool, sprinkler-protected, ventilated area. The storage temperature must be maintained below 54°C.
   - o Storage area must be isolated from other hazardous and combustible material. The area is to be used for only new lithium batteries.
   - o Storage of lithium batteries or equipment containing lithium batteries in berthing areas is prohibited.

   Spent or depleted lithium batteries or equipment with such batteries installed must be stored on the weather deck:
   - o Reusable lithium batteries must be packaged in original containers and stored in a drip-proof, self-draining ventilated

metal locker with the capability to maintain temperatures below 54°C (130°F).

- o The locker must be isolated from other hazardous items and be used only for the storage of depleted lithium batteries or equipment with depleted lithium batteries installed.
- o Non-reusable lithium batteries should be stored in the same lockers as above. If storage space is not available, non-reusable lithium batteries must be stored on the weather deck in the original packaging containers. This storage area must be isolated and posted with warning placards.

The U.S. Navy imposes additional requirements upon those services using lithium batteries which, when new, were approved for use based upon testing other than that prescribed in NAVSEANOTE 9310. These requirements are summarized below:

- o Prior to ashore deployment of equipment using lithium batteries, mating the batteries to the equipment aboard ship must be conducted only in weather deck locations.
- o Following completion of each ashore deployment, used or depleted lithium batteries or equipment containing lithium batteries installed must be stored on the weather deck, as previously discussed.
- o All used lithium batteries must be offloaded at the earliest possible time. Under no circumstances are the batteries to be offloaded during ammunition or refueling operations.
- o Spent lithium batteries from ashore deployment or from use while underway are disposed of by discharge overboard in water depths in excess of 100 fathoms (183 m) outside the 50 mile (82 km) limit. These waste lithium batteries shall not be stowed for shore disposal.
- o Ashore storage of lithium batteries and equipment containing lithium batteries is the responsibility of the cognizant service organization.

It is believed[31] that the potential for a lithium battery fire to start in a properly packaged unit is no greater than for ordinary combustible material.

Should a lithium battery be involved in a fire, an "extra hazard"[31] would exist due to the difficulty associated with extinguishing burning lithium metal. Only such Class D extinguishers as the Met-L-X or Lith-X type are effective in combating these fires.[28,29] In practice, however, lithium battery fires can be extinguished by the application of copious amounts of water. Though lithium reacts violently with water, sufficient quantities of water will significantly reduce the potential hazards by extinguishing combustible packaging materials. The net effect is a rapid cooling of the batteries, thereby minimizing the possibility for further cell venting and spread of the fire to other areas of the storage facility. A lithium metal fire will be expended quickly.[8,28] It is estimated that complete combustion of the lithium from a BA-5590/U, comprised of ten lithium-sulfur dioxide D cells, will last less than five minutes. The U.S. Navy requires the use of an air respirator or a self-contained breathing apparatus approved by the National Institute for Operation Safety and Health (NIOSH) in situations in which vented gases may be present.[12,13]

DISPOSAL

Until the early 1980's, several methods were used or were recommended for the disposal of waste lithium batteries. These methods included: a) disposal in secure or sanitary landfills, b) disposal in monitored and controlled disposal ponds, c) incineration, d) burial of lithium batteries cast in concrete, and e) "neutralization" of cell contents by disassembly with subsequent exposure to a humid atmosphere.[6,8,32,33] In 1982, the Environmental Protection Agency (EPA) sponsored a study at Factory Mutual Research Corporation to determine the hazards associated with the disposal of waste lithium batteries.[34] This study focused on the potential hazards for workers handling the batteries and the longterm effects to the environment caused by conventional solid waste disposal practices. Vincent[34] concluded that: a) $Li-SO_2$ and $Li-SOCl_2$ batteries be classified as hazardous to personnel since instances of explosions, fires, and ventings of toxic fumes are possible during these disposal operations, b) under similar disposal operations, $Li-(CF_x)_n$, Li-FeS, $Li-FeS_2$, $Li-MnO_2$, Li-CuO, $Li-I_2$, $Li-V_2O_5$ and $Li-Ag_2CrO_4$ batteries do not pose as great a safety hazard to personnel as $Li-SO_2$ or $Li-SOCl_2$ batteries, c) incineration of all lithium

batteries should be prohibited due to the hazard potential relative to both the personnel and the environment, and d) contamination of the environment over the longterm is possible as a result of the release of toxic materials contained in the $Li-SO_2$, $Li-SOCl_2$, $Li-I_2$, $Li-(CF_x)_n$, $Li-V_2O_5$, and $Li-MnO_2$ battery systems.

As use of the lithium-sulfur dioxide batteries by the U.S. Army increased during the early 1980s, a major concern of the Army and the Defense Logistics Agency (DLA) involved the proper disposition of accumulated waste lithium batteries. A response to a number of requests for guidance on the regulatory status of waste $Li-SO_2$ batteries was issued by the EPA on March 7, 1984.[35] It was determined that waste $Li-SO_2$ batteries did exhibit four of the characteristics for reactive solid wastes in accordance with Section 261.23 of Title 40, Code of Federal Regulations, Protection of Environment (40 CFR 261.23).[36] These characteristics were concluded to be: a) waste $Li-SO_2$ batteries form potentially explosive mixtures with water (40 CFR 261.23 (a) (3)), b) When mixed with water, waste $Li-SO_2$ batteries generate toxic gases, vapors, or fumes in a quantity sufficient to present a danger to human health or the environment (40 CFR 261.23 (a) (4)), c) waste $Li-SO_2$ batteries are cyanide- or sulfide-bearing waste which, when exposed to pH conditions between 2 and 12.5, can generate toxic gases, vapors, or fumes in a quantity sufficient to present a danger to human health or the environment (40 CFR 261.23 (a) (5)), and d) waste $Li-SO_2$ batteries are capable of detonation or explosive reaction if they are subjected to a strong initiating source or if heated under confinement (40 CFR 261.23 (a) (6)). In view of the above, landfilling of waste $Li-SO_2$ batteries is prohibited unless the waste batteries are treated, rendered, or mixed such that they no longer exhibit any characteristic for a reactive solid hazardous waste.

The opinion rendered by the EPA[35] specifically relates to $Li-SO_2$ batteries and declines comment on other lithium battery systems due to a lack of information. Many users and manufacturers have determined that waste batteries for these systems would also exhibit at least one characteristic of reactivity. As a result, the EPA opinion is being interpreted as a required treatment program for waste batteries of several other lithium battery systems.[23]

The Hazardous and Solid Waste Amendments of 1984 (bill H.R. 2867) to amend

the Solid Waste Disposal Act was adopted in October, 1984.[37] Section 222 (e) (2) required the EPA to respond within 15 months after enactment of H.R. 2847 as to whether spent lithium batteries should be listed as hazardous waste in section 222 (b) (1). Such a listing would require that spent lithium batteries be subjected to hazardous waste regulations. No response was given by the EPA in addition to the rendered opinion on waste Li-SO_2 batteries and the evaluation of other lithium battery systems against the eight reactivity characteristics as specified in 40 CFR 261.23. Sections 221 (d) (1) through 221 (d) (9) of the Hazardous and Solid Waste Amendments of 1984 lowered the limits for Small Quantity Generator Waste from a total quantity of hazardous waste of 1000 kg to a total quantity of hazardous waste of 100 kg at any one location during a calendar month. The above standards "may vary from the standards applicable to hazardous waste generated by larger quantity generators, but such standards shall be sufficient to protect human health and the environment."

Battery Disposal Technology (BDT) Incorporated is the only fully permitted disposal facility in the United States specifically established for the treatment of waste lithium batteries. In 1979, the basic concept for the treatment method was formulated as a result of meetings among Belstadt (T.H.), Krehl, Liang and Murphy of Electrochem Industries and Zajac of BDT. Belstadt (J.A.) of Electrochem designed, fabricated, and optimized equipment which simultaneously punctured and crushed waste lithium cells. The opened cells then dropped into a neutralizing solution contained in a metal drum. After sufficient quantities of cells were hydrolyzed in this manner, vermiculite was added to create a thick, uniform slurry. Finally, the contents were thoroughly admixed with concrete and the resultant mixture was allowed to solidify. The drums were transported to a sanitary landfill for final disposal.

Zajac, Cohen, and Kautz expanded the above treatment process in order to accomodate larger quantities of both cells and batteries. Zajac also obtained the appropriate permits from the EPA and the New York State Dept. of Environmental Conservation for full-scale operation of the facility. Lithium cells and batteries enter into a hammermill via a conveyor system.[23] The action of the hammermill breaches cell cases and exposes the cell contents to a neutralizing aqueous solution. This process takes place in an explosion proof

room. Further operation of the hammermill reduces the metal and other solid materials to a size small enough to pass through a sieve. Both solids and liquids are then retained in a holding tank to ensure completion of the hydrolysis reactions. After filtering, both the solid and liquid residues of the process are properly disposed.

The costs for the treatment and disposal of waste lithium batteries vary and are dependent upon the lithium battery chemistries. For example, the price, exclusive of taxes, packaging, and transportation, for the treatment and disposal of $Li-SO_2$ batteries range from about \$3 per pound (\$6.60 per kg) for large quantities to about \$4.50 per pound (\$10 per kg) for small quantities.[38] Corresponding prices for $Li-SOCl_2$ batteries vary from about \$3.50 per pound (\$7.70 per kg) to more than \$5.00 per pound (\$11.00 per kg). The expenses associated with packaging and transportation of waste lithium batteries significantly increases the total cost for battery disposal. Dampier[27] cites a total disposal cost of \$160 per 30 gallon barrel containing a maximum amount of six pounds of waste lithium batteries, corresponding to about \$26.67 per pound (\$58.67 per kg).

In view of the disposal costs and the difficulties in maintaining waste storage facilities, studies at LABCOM, Fort Monmouth, are being conducted to treat spent lithium-sulfur dioxide batteries so that they no longer exhibit any characteristic of a reactive solid hazardous waste.[39] A number of methods are being investigated to ensure the complete discharge of $Li-SO_2$ batteries procured in accordance with MIL-B-49430(ER). Such batteries are comprised of cells of the balanced electrochemical design (lithium to sulfur dioxide ratio of 1.1 ± 0.1). Once a proper procedure is developed, the U.S. Army will seek approval from the EPA to dispose of the batteries in a sanitary landfill.

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CHAPTER 4

CONCLUSIONS AND RECOMMENDATIONS

INTRODUCTION

The objectives of this report were a) to determine the safety characteristics for several lithium primary and secondary battery systems and b) to evaluate these systems as regards the deployment of specific cells and batteries in the fleet without the required electrical and thermal abuse tests as prescribed in NAVSEANOTE 9310. It is important to note that the results of this study strictly pertain to lithium cell and battery usage by the U.S. Navy and other U.S. military establishments and may not be appropriate for commercial or consumer applications.

The widespread acceptance of lithium battery systems has been hampered by the misconception that all lithium cells and batteries are intrinsically hazardous. This impression has been fostered, to a large extent, by the widely publicized accounts describing instances of venting, fire, or explosions involving lithium-sulfur dioxide (Li-SO_2), lithium-thionyl chloride (Li-$SOCl_2$), and lithium-chlorine in sulfuryl chloride (Li-Cl_2 in SO_2Cl_2) cells and batteries (Table 1, Chapter 1). The majority of these accidents caused structural damage and/or personal injury. Intense research and development efforts over the past five to seven years have resulted in a marked decrease in both the total number and the severity of the accidents.

Few instances of cell venting, fires, or explosions have occurred for lithium-solid cathode and lithium-solid electrolyte cells and batteries under normal use conditions. For example, no safety related incidents have been reported[1] for the lithium-polycarbonmonofluoride (Li-$(CF_x)_n$) battery comprised of two Panasonic Br-2/3A size cells connected in series. This battery has found

widespread consumer usage in the Kodak Disc Camera. Further, the medically implantable-grade lithium-iodine ($Li-I_2$) cell is considered to be among the safest of <u>any</u> electrochemical power source.[2] It is important to note that cells and batteries of both the lithium-solid cathode and the lithium-solid electrolyte systems will explode violently if subjected to abuse conditions of sufficient severity to fuse the low melting lithium anode material (melting point: 180.5°C), thereby creating an uncontrolled thermal runaway chemical reaction. Thus, explosions will result when the $Li-I_2$ pacemaker cell is subjected to such abuse tests as incineration/localized heating charge, or forced overdischarge at amperage levels many times in excess of the rate capability of the system.

Several other important factors must be considered in the evaluation of the overall safety characteristics for any particular lithium battery system or for any specific cell size or design. These factors include: a) the total lithium content per cell or battery, b) the toxicity, flammability, and stability of cell components and cell reaction products, c) the electrochemical balance and internal cell design, d) the thermal management characteristics for lithium cells and batteries of all sizes discharged at moderate to high rates, e) tolerance to electrical, thermal, and physical abuse, and f) the incorporation of such safety features as vents, thermal and electrical fuses, diodes, and hermetic seals. All primary and secondary lithium systems were evaluated relative to those applicable safety related factors given above.

GENERAL RECOMMENDATIONS

Throughout the course of this study, it became increasingly apparent that specific test conditions or other considerations, as regards the overall systems safety for many U.S. Navy applications, should be retained or implimented:

<u>General recommendation 1</u>: The High Temperature Test as described in Enclosure 2 of NAVSEANOTE 9310[3] shall be retained to enable congnizant U.S. Navy personnel the capability to assess the safety characteristics and hazards associated with worst case conditions. This test is specifically designed to account for the hazards attendant with massive internal short circuits, thermal runaway conditions due to the creation of internal hot spots, intercell short circuits which bypass electrical fusing devices in a series string, and explosions caused by rapid side reactions within the cell. The above hazard conditions cannot be

simulated by any other test procedure. It is also important to note that this test procedure also serves as the most appropriate method to assess the effects of a rapid pressure increase for both the operation of the pressure relief valve mechanism and total containment capability in the end item. The overall criteria for pass/fail of a proposed end item depends, to a large extent, upon the capability of the end item unit to withstand internal pressures of up to 50% of the failure pressure or yield strength of the end item unit. End items destined for use aboard submarines must exhibit total containment under these criteria. Generally, only one or two cells of a multicell battery may vent or explode under such electrical abuse conditions as short circuit, forced overdischarge, or charge. The probability for several cells to fail nearly simultaneously is significantly greater under High Temperature Test conditions.

General recommendation 2: Specific test procedures shall be developed to more accurately assess the safety characteristics for such specialized power supplies as the reserve and thermal batteries. The electrical and thermal abuse tests described in Enclosure 2 of NAVSEANOTE 9310 relate to activated primary lithium cells and batteries. As such, present test procedures cannot fully determine the hazards associated with the unique characteristics for either the reserve or the thermal battery designs. Specific areas of safety concern relative to the reserve batteries include: a) inadvertent activation during quiescent or abuse conditions. Some, but not all, reserve battery designs incorporate a valve to vent the electrolyte to the external environment when the reservoir reaches a certain temperature. Simultaneously, a high pressure relief valve to the cell stack will also be vented., b) intercell or manifold growth of lithium dendrites as a result of prolonged wet stands under open circuit conditions. Some, but not all, reserve batteries comprised of either the bipolar or conventional cell design possess long electrolyte leakage paths., c) mechanical damage or inadvertent activation caused by such physical abuse as shock, vibration, dropping, crushing, and penetration by an electrically conductive device, and d) the effect of rapid electrolyte entry at activation into the cell stack on the integrity of electrode structure (internal short circuits, intercell connections, etc.).

Reserve batteries will generally possess thermal and electrical fuses within the cell stack. Thus, short circuit and forced overdischarge testing in strict accordance with the procedures in Enclosure 2 of NAVSEANOTE 9310 may be

ineffective in accurately assessing the hazards attendant with these abuse conditions.

Specific areas of concern relative to thermal batteries include: a) inadvertent activation during quiescent or thermal abuse conditions, and b) case rupture as a result of abuse test conditions, internal construction defects, glass to metal seal failure, or damage caused by physical or handling abuse. In general, thermal batteries possess extremely high rate capabilities. Therefore, it can be seen that electrical abuse testing (including charging) in accordance with Enclosure 2 of NAVSEANOTE 9310 may not be a practical approach to an accurate assessment of the hazards associated with thermal battery systems.

It is important to note that cognizant U.S. Navy personnel are aware of the deficiencies of the tests prescribed in NAVSEANOTE 9310 relative to both the lithium reserve and lithium thermal batteries. As a result, procedures are presently being developed to more accurately determine the safety characteristics for these designs. The next issue of NAVSEAINST 9310.1B[4] will contain these test procedures.

General recommendation 3: The majority of U.S. Navy applications require high energy densities at high power levels. As a result, most of the lithium cell and battery use and safety experience concerns the Li-SO_2, Li-$SOCl_2$, and Li-Cl_2 in SO_2Cl_2 primary systems. In contrast, only limited testing in accordance with the abuse procedures given in Enclosure 2 of NAVSEANOTE 9310 has been performed with either the lithium-solid cathode or lithium-solid electrolyte cells and batteries. In general, these systems possess low rate capabilities and do not pose a thermal runaway or explosion hazard when small cells and batteries are subjected to short circuit conditions. However, exposure of the cells and batteries to thermal abuse or electrical charging conditions could lead to either violent ventings or explosions. In addition to the above hazards, some lithium-solid cathode systems contain electrolyte solutions comprised of flammable solvents or the unstable solute, lithium perchlorate ($LiClO_4$).[5] Solvents such as 1,3 dioxolane, tetrahydrofuran, methyl formate, and methyl acetate are considered fire or explosion hazards[6-8] when exposed to heat or flame, while dimethoxyethane is considered to be a moderate fire or explosion hazard. The solvents, propylene carbonate and gamma-butyrolactone are considered slight hazards.[6] Lithium perchlorate ($LiClO_4$) poses moderate fire and explosion hazards due to shock, exposure to heat, or chemical reaction.[6] This salt will

also emit highly toxic chlorides when heated and will react violently with reducing materials such as lithium metal.[6] In view of the above, lithium-solid cathode cells containing $LiClO_4$ as the electrolyte salt shall be subjected to the constant current discharge/reversal test and the charging test (when appropriate) given in Enclosure 2 of NAVSEANOTE 9310. The safety review shall determine whether lithium-solid cathode cells containing a flammable solvent would be considered to be "extra hazardous" after examination of the results of the high temperature tests (i.e., whether solvent fires contribute significantly to or initiate the burning of lithium metal with the subsequent release of highly toxic lithium oxide and lithium hydroxide fumes).

SPECIFIC RECOMMENDATIONS

A study to determine the safety characteristics for lithium primary and secondary battery systems has been conducted. Specific recommendations are given for each lithium electrochemical systems as to whether cells (or batteries) should be subjected to the formal test program detailed in Enclosure 2 of NAVSEANOTE 9310. Such factors as cell size, internal constructional design, safety features, total lithium content per cell, and system maturity were considered in these analyses. In addition to the data obtained from the open technical literature and those contributed by the manufacturing, governmental, and user sectors (Tables 3 and 4, Chapter 1), a significant amount of key information regarding the specific performance characteristics and constructional features for lithium cells was acquired from the works of Shuler and Wharton.[9,10] The Underwriters' Laboratories reports[11] detailing the results of electric, thermal, and mechanical abuse testing performed upon single cells submitted for Component Recognition were also a consideration in these recommendations. Data relative to the toxicity and flammability of cell constituents were obtained from Sax,[6] Vincent,[7], and Mackison, Stricoff, and Patridge.[8]

MAJOR PRIMARY LITHIUM BATTERY SYSTEMS

Lithium-Copper Oxide Systems[12-15]
Li-CuO and Li-$Cu_4O(PO_4)_2$

SAFT manufactures both the Li-CuO and Li-$Cu_4O(PO_4)_2$ cells for commercial and military applications. Currently, five sizes of Li-CuO cells are available: a) the LC 07, ½ AA size bobbin cell, b) the LC 02, ½ AA size bobbin cell, c) the LC 6, AA size bobbin cell, d) the LCH 14, C size, spiral wound, and e) the LCH 20, D size spiral wound. Three types of Li-$Cu_4O(PO_4)_2$ cells are available: a) the LCP 6, AA size bobbin cell, b) the LCP 6 HT, AA size, bobbin cell for high temperature applications, and c) the LCP 14 HT, C size, bobbin cell for high temperature applications.

<u>Recommendation</u>: Short circuit tests shall not be required for the bobbin cells of either type. The Li-CuO spirally wound C size (LCH 14) and D size (LCH 20) shall be subjected to short circuit testing. Forced overdischarge and charge abuse tests will result in cell explosions for both the Li-CuO and Li-$Cu_4O(PO_4)_2$ types unless diode protection is provided.[16] In addition, the typical electrolyte is comprised of $LiClO_4$ in 1,3 dioxolane (see General recommendation 3). Therefore, cells and batteries of both Li-CuO systems shall be required to undergo the forced overdischarge, charge (if applicable), high temperature, and electrical safety device tests given in Enclosure 2 of NAVSEANOTE 9310.

<u>Manufacturer</u>: SAFT

<u>Toxicity</u>: $LiClO_4$ will emit highly toxic chlorides when heated.

<u>Flammability</u>: 1,3 dioxolane is a fire/explosion hazard in contact with heat or flame.

$LiClO_4$ - see General recommendation 3

Lithium-Manganese Dioxide[17-24]
Li-MnO_2

Various types of lithium-manganese dioxide cells and batteries are produced for use in such commercial and consumer applications as business machines, calculators, watches, and photographic equipment. Several cell designs are commercially available from manufacturers:

1. Button cells

The standard Li-MnO_2 button cells, designed for low rate applications, are comprised of one pressed powder MnO_2 cathode and one lithium anode. High rate Li-MnO_2 button cells consist of two lithium anodes on either side of a thin, pasted MnO_2 cathode. Typically, both cell types possess crimped plastic or plastic grommet seals. Power Conversion Inc., however, produces a hermetic cell, the MDX200A, having a glass-to-metal seal. All currently available standard and high rate Li-MnO_2 button cells are given in the lists on pages 70 and 71, respectively.

2. Cylindrical cells

The internal design for cylindrical Li-MnO_2 cells may consist of either the spirally wound or the bobbin structures. The majority of the cells listed for the cylindrical cells are of the spirally wound design and possess crimped plastic or plastic grommet seals. Sanyo Electric does manufacture several hermetically sealed cell models in sizes from the ANSI ½AA to the C size as well as one oval shaped cell (CR736E-2). Currently available Li-MnO_2 cylindrical cells with crimped plastic and laser welded seals are listed on pages 72 and 73, respectively.

3. Standard Li-MnO_2 batteries

Several manufacturers produce a battery comprised of two spirally wound CR-1/3N cells electrically connected in series for use in photographic equipment. In addition, Ultra Technologies (Kodak) will soon manufacture a NEDA 1604L nine volt "transistor" battery for such consumer applications as smoke alarms, portable radios, and toys. Both Duracell and Ultra Technologies offer a six volt battery for use in photographic applications. Commercially available Li-MnO_2 batteries are listed on page 74.

Button Cells

A. Button Li-MnO_2 cells having crimped or plastic grommet seals; one Li anode, one pressed powder MnO_2 cathode.

Sanyo Cell Model Number	Duracell, USA Designation	General Electric Designation	Panasonic Designation	SAFT America Designation	Union Carbide Designation	Varta Batteries Designation	Venture Technologies Designation	Approx. Nominal Capacity, mAh
---			CR1216					25
CR1220	DL1220	X	X			X		30
---			CR1616					50
CR1620	DL1620	X				X		50
CR2016	DL2016	X	X		X	X	LIM2016	60
CR2316						X		90
---				LM2020				90
---							LIM2320	110
CR2025	DL2025	X	X		X	X		120
CR2420	DL2420	X				X		120
CR2032	DL2032	X	X		X	X	LIM2032	170
CR2430	DL2430	X				X		200
---				LM2425				200

NOTE: 1. The letter "X" denotes identical cell model numbers as those given for the Sanyo cells.

2. All Sanyo, Duracell, General Electric, and SAFT cells listed above are accepted in the UL Component Recognition and Follow-Up Service. Panasonic (Matsushita Electric) CR-2016, -2025, and -2032 cells are UL Recognized Components; Union Carbide CR-2016 and -2025 cells are UL Recognized Components. SAFT cell models 40LH220 and 40LF220 are also UL Recognized Components and consist of LM2425 cells with plastic covers. The two cell models allow for horizontal (40LF220) or vertical (40LH220) mounting on an IC board.[11A]

3. Operational temperature ranges - Sanyo and Varta cells: -20 to +60°C
Duracell, GE, SAFT, and Venture Technology cells: -20 to +50°C
Panasonic cells: -10 to +60°C
Union Carbide cells: -60 to +75°C

4. All of the above cell models possess positive case (can) polarities.

B. Button, high rate Li-MnO_2 cells having crimped or plastic grommet seals; two Li anodes, one pasted MnO_2 cathode.

Sanyo Cell Model Number	General Electric Designation	Approximate Nominal Capacity, mAh
CR2016H		60
CR2025H	X	100
CR2420H	X	120
CR2032H	X	130
CR2430H	X	160

NOTE:
1. The letter "X" denotes identical cell numbers as those given for Sanyo cells.
2. The operating temperature range for Sanyo high rate button cells is -20 to +60°C, that for General Electric high rate button cells is -20 to +50°C.
3. All of the above cells possess positive case (can) polarities.

Cylindrical Cells

A. Spirally wound $Li-MnO_2$ cylindrical cells having crimped plastic or plastic grommet seals (hermetic and non-hermetic).

Sanyo Cell Model Number	Duracell USA Designation	General Electric Designation	Ultra Technologies (Kodak) Designation	Union Carbide Designation	Varta Designation	Venture Technologies Designation	Approximate Nominal Capacity, Ah	ANSI Size
CR772		X					0.03	mini
CR333		X					0.04	pin
CR-1/3N	DL-1/3N	X	K58L	2L76	X	LIM110	0.16	1/3N
CR-2N	DL-2N	X			X		1.0	2N
---	DL-2/3A					LIM163	1.1	2/3A
---					CR-2NP		1.4	2N
---						LIM165	1.6	A
---						LIM255	4.8	C
---						LIM336	10.0	D

NOTE:
1. The letter "X" denotes identical cell model numbers as those given for Sanyo cells.
2. The Sanyo and General Electric CR333 pin cell is of bobbin cell design having a positive case polarity except the CR-2N, DL-2N, DL-2/3A, and the CR-2NP cells.
3. All Sanyo, Duracell, and General Electric $Li-MnO_2$ cells given above are UL Recognized Components.[11A]
4. The operational temperature ranges for the above cells correspond to those given for the $Li-MnO_2$ button cells.

B. Hermetically sealed (laser welded) $Li\text{-}MnO_2$ cylindrical, oval, or button cells:

Sanyo Cell Model Number	Power Conversion, Inc. Model Number	ANSI Size	Cell Type	Nominal Capacity, Ah
CR736E-2		---	oval	0.07
CR14250SE		1/2AA	cyl.	0.75
CR12600SE		2N	cyl.	1.4
CR17335SE		2/3A	cyl.	1.7
CR17450SE		A	cyl.	2.2
CR23500SE		C	cyl.	4.5
---	MDX200A	---	button	0.2

NOTE: 1. Sanyo cell models CR14250SE, CR12600SE, and CR17335SE are UL Recognized Components.[11A]

2. The operational temperature range for the Sanyo cells listed above is -40 to +85°C; the operational temperature range for the PCI cell is -20 to +70°C.

3. All Sanyo cells possess positive case polarities. The PCI MDX200A cell is case negative polarity.

Standard Li-MnO Batteries

Sanyo Number	Duracell Number	General Electric Number	Ultra Technologies (Kodak) Number	Union Carbide Number	Varta Number	OCV, V	Nominal Capacity, mAh
2CR-1/3N	PX28L	X	K28L	L544	X	6.6	160 to 200
---			U9VL			9.9	1100
---	DL223L		K223L			6.6	1200

NOTE: 1. The letter "X" denotes identical battery model numbers as those given for the Sanyo 2CR-1/3N battery.

2. The Duracell PX28L battery is a UL Recognized Component.[11A]

3. Operational temperature ranges:

Duracell and General Electric $Li-MnO_2$ batteries: -20 to +50°C

Sanyo $Li-MnO_2$ battery: -10 to +60°C

Varta $Li-MnO_2$ battery: -20 to +60°C

Ultra Technologies (Kodak) $Li-MnO_2$ batteries: -20 to +45°C

4. Specialty cells and batteries

Sanyo Electric has developed several prismatic Li-MnO_2 cells which could serve as component cells for large Li-MnO_2 batteries. For example, the LM20 and LM120 cells yield realized capacities of 20 and 120Ah, respectively, and are currently under further development as power supplies for communication applications.

All Li-MnO_2 cell and battery manufacturers, with the exception of Union Carbide Corporation, use an electrolyte solution of lithium perchlorate solute in a mixed solvent of propylene carbonate and dimethoxyethane (see General recommendation 3). The electrolyte for Union Carbide Li-MnO_2 cells and batteries consists of a less powerful oxidizing agent, lithium trifluoromethylsulfonate, $LiCF_3SO_3$, dissolved in the mixed solvent of propylene carbonate and dimethoxyethane. The use of this electrolyte solution in Li-MnO_2 cells and batteries not only mitigates the safety-related concerns relative to $LiClO_4$, but also improves the low temperature discharge performance.

Several manufacturers have incorporated a safety vent feature in the design of cells and batteries:

1. All General Electric and Sanyo Li-MnO_2 cells and batteries possess resealable vent structures in the anode cap (button cells) or cell top (cylindrical cells).
2. All Duracell Li-MnO_2 cells and batteries possess coined or stamped weakened areas in the bottoms of the case.
3. All Matsushita (Panasonic) Li-MnO_2 cells and batteries have plastic cell covers which weaken at elevated temperatures.
4. Varta cells CR-1/3N and CR-2N as well as the 2CR-1/3N battery possess a puncturable diaphragm in the cylinder top. No other Varta cells have a means for venting.
5. Lithium-manganese dioxide cells and batteries produced by Power Conversion, Inc., SAFT America, Union Carbide Corporation, or Venture Technologies, Inc. do not employ safety vents.

   No electrical fuses are incorporated into the internal structures of any Li-MnO_2 cells listed in this discussion.

Recommendations:

1. Single cells as power supplies -

All low and high rate Li-MnO_2 button cells, the cylindrical cells corresponding to the Sanyo/IEC designations of CR772, CR333, CR-1/3N, and the CR736E-2 oval cell which are used as sole sources of power shall be exempt from all tests prescribed in Enclosure 2 of NAVSEANOTE 9310, with the exception of the High Temperature Test. Low and high rate button cells and cylindrical cells having nominal capacities of 90mAh to 200mAh shall incorporate an electrical fuse of an appropriately low current value in the positive lead.

All low and high rate button cells, the cylindrical cells corresponding to the Sanyo/IEC designations of CR772, CR333, CR-1/3N, and the CR736E-2 oval cell which are used as support power supplies to a mains (DC) power supply shall be exempt from all tests prescribed in Enclosure 2 of NAVSEANOTE 9310, with the exception of the High Temperature Test provided a) an electrical fuse of an appropriately low current value is located in the negative lead, and b) the positive lead of the battery is equipped with redundant diode protection. Such protection may also be achieved through use of either an electrical fuse or a resistor located between a single diode and the mains (DC) power supply. It is important to note that the values for either the fuse or the resistor should be selected to limit any possible charging current to less than 1mA in the event of diode failure.

All other cylindrical cells having nominal capacities greater than 0.5Ah and less than or equal to 2.2Ah (ANSI sizes 1/2AA, 2N, 2/3A, and A) shall only be exempt from the Short Circuit Test. All other applicable tests prescribed in Enclosure 2 of NAVSEANOTE 9310 shall be conducted.

Lithium-manganese dioxide C,D, and specialized cells (e.g., LM20 and LM120) shall be subjected to all applicable tests prescribed in Enclosure 2 of NAVSEANOTE 9310.

2. Batteries comprised of <u>two</u> Li-MnO_2 cells as power supplies -

Batteries with two identical cells of the group comprised of all low and high rate button cells, the cylindrical cells corresponding to the Sanyo/IEC designations of CR772, CR333, CR-1/3N (including the commercially available 2CR-1/3N battery), and the CR-736E-2 oval cell which are used as sole sources of power shall be exempt from all tests prescribed in Enclosure 2 of NAVSEANOTE 9310, with the exception of the High Temperature Test. Batteries comprised of two button cells, two cylindrical cells, or two oval cells shall incorporate an electrical fuse of an appropriately low current value and a thermal fuse in the negative (ground) lead. Batteries comprised of two cells electrically connected in parallel shall also incorporate blocking diodes in each positive lead.

When the above batteries are used as support power supplies to a mains (DC) power supply, such batteries shall be exempt from all tests prescribed in Enclosure 2 of NAVSEANOTE 9310, with the exception of the High Temperature Test, provided a) the battery possesses the electrical and thermal protective devices as described above, and b) the positive lead of the battery is equipped with redundant diode protection. Such protection may also be achieved through use of either an electrical fuse or a resistor located between a single diode and the mains (DC) power supply. It is important to note that the values for either the fuse or the resistor should be selected to limit any possible charging current to less than 1mA in the event of diode failure.

Batteries comprised of two cells from the group of cylindrical cells having nominal capacities of 0.5Ah to 2.2Ah shall be subjected to <u>all</u> applicable tests prescribed in Enclosure 2 of NAVSEANOTE 9310.

Batteries comprised of two lithium-manganese dioxide C, D, and specialized cells shall be subjected to <u>all</u> applicable tests prescribed in Enclosure 2 of NAVSEANOTE 9310.

3. Batteries of three cells or more -

Batteries comprised of three or more cells, regardless of design or nominal capacity (lithium content), shall be subjected to all applicable tests prescribed in Enclosure 2 of NAVSEANOTE 9310.

Manufacturers: Duracell, U.S.A.
General Electric Company
Matsushita Electric Industrial Co., Ltd.
(Panasonic Industrial Company)
Power Conversion Inc.
SAFT America
Sanyo Electric Co., Ltd.
Ultra Technologies, Inc. (Eastman Technology, Inc.)
Union Carbide Corporation
Varta Batteries, Inc.
Venture Technologies, Inc.

Toxicity:

1. Manganese dioxide (MnO_2) is highly toxic only when injected intravenously.
2. Lithium perchlorate ($LiClO_4$) will emit highly toxic chlorides when heated.
3. Lithium trifluoromethylsulfonate will emit highly toxic SO_x fumes when heated to decomposition or exposed to acids.

Flammability:

1. Propylene carbonate and dimethoxyethane are slight and moderate fire hazards, respectively.
2. $LiClO_4$ - see General recommendation 3.

Lithium-Polycarbon Monofluoride[25-32] $Li-(CF_x)_n$

Eagle Picher Industries, Inc.

The Electronics Division of Eagle-Picher produces the KEEPER lithium-polycarbon monofluoride $Li-(CF_x)_n$ cells and batteries which are specifically designed as power supplies for Complementary Metal Oxide Semiconductor (CMOS) memory support applications. The basic, non-standard cell features an internal prismatic construction, a glass-to-metal seal, and welded hermetic closure. This cell and batteries comprised of this cell do not possess electrical fuses or venting mechanisms. Glass-to-metal seal failure is intended to serve as the only means to relieve the high internal pressures attendant with some abuse conditions. All cells and batteries listed below are accepted as Recognized Components by Underwriters Laboratories (UL):[11B]

A. Cells

Model Number	Height, cm	Width, cm	Thickness, cm	Nominal Capacity, Ah	Maximum Recommended Discharge Rate, mA
LDFS-5PN	2.54	1.65	0.64	0.5	10
LDFS-5P	3.05	1.78	0.84	0.5	10

B. Batteries

Model Number	Height, cm	Width, cm	Thickness, cm	OCV, V	Nominal Capacity, Ah	Maximum Recommended Discharge Rate, mA
LDFS-5PMP	3.81	3.05	0.84	3.0	1.0	20
LDFS-5PMS	3.81	3.05	0.84	6.0	0.5	10

NOTE:
1. The operational temperature range for the above cells and batteries is -73 to +93°C.
2. Model LDFS-5PN is the basic component cell for model LDFS-5P (a LDFS-5PN cell potted into a plastic cover jacket) and battery models LDFS-5PMP and LDFS-5PMS.
3. Battery model LDFS-5PMP is comprised of two LDFS-5PN cells electrically connected in parallel; battery model LDFS-5PMS is comprised of two LDFS-5PN cells electrically connected in series.

Recommendation:

1. Models LDFS-5PN and LDFS-5P single cells shall be exempt from the tests prescribed in Enclosure 2 of NAVSEANOTE 9310, with the exception of the High Temperature Test, provided a) each cell is the sole power supply for the application, b) each cell possesses an electrical fuse of low current value (e.g., 0.1A) located in the positive lead, and c) each cell incorporates a thermal fuse designed to interrupt the circuit at temperatures of 89 to 95°C. The thermal fuse shall be located as closely as possible to the cell.
2. A single series-connected string of cells selected from models LDFS-5PN or LDFS-5P which serves as a sole power supply shall be exempt from the tests prescribed in Enclosure 2 of NAVSEANOTE 9310, with the exception of the High Temperature Test, provided a) the required discharge current is less than five (5) mA, b) the series string of cells possesses an electrical fuse of low current value (e.g., 0.1A) located in the negative lead, and c) the series string of cells incorporates a thermal fuse designed to interrupt the circuit at temperatures of 89 to 95°C. The location of the thermal fuse shall be in the negative lead either between adjacent cells or in the geometric center of a group of series-connected cells.
3. Batteries comprised of cells or series strings of cells (from Models LDFS-5PN or LDFS-5P) which are, in turn, electrically connected in parallel shall be exempt from the tests prescribed in Enclosure 2 of NAVSEANOTE 9310, with the exception of the High Temperature Test, provided a) these batteries are the sole power sources, b) the required discharge rate is less than the quantity (5 mA x number of cells or series strings of cells connected in parallel), c) each cell or series string of cells shall incorporate an appropriate blocking diode in the positive lead to prevent the inadvertent electrical charging of a depleted cell or series string of cells by other cells or series string of cells, respectively, in the battery, and d) the battery shall incorporate the appropriate electrical and thermal fusing, as described above, in the negative (ground) lead of the battery.
4. Cells and batteries which fulfill the descriptions of 1 through 3, above, and which serve as back-up power supplies to a mains (DC) power

supply shall be exempt from the tests prescribed in Enclosure 2 of NAVSEANOTE 9310, with the exception of the High Temperature Test, provided the positive lead of the cell or battery is equipped with redundant diode protection. Such protection may also be achieved through use of either an electrical fuse or a resistor located between a single diode and the mains (DC) power supply. It is important to note that the values for either the fuse or the resistor should be selected to limit any possible charging current to less than 5mA in the event of diode failure.

Eagle-Picher also manufactures a 175 gram, spirally-wound Li-$(CF_x)_n$ cylindrical cell, model LCFS-20, with dimensions of 3.05 cm diameter and 14.0 cm height. This nonstandard cell possesses a diameter slightly less than that for the ANSI DD cell (3.4 cm) and a height greater than the standard ANSI DD cell (11.3 cm). This cell features negative case polarity, a welded hermetic closure, a glass-to-metal seal, and an internal electrical fuse. The operational temperature range for this cell is -70 to +60°C. No venting mechanism is incorporated into the cell design.

Cell Model	Nominal Capacity, Ah	Discharge Current, A	Maximum Recommended Discharge Rate, A
LCFS-20	20 to 25	0.5	1.5

Recommendation: The LCFS-20 cell and batteries constructed from the LCFS-20 cell (e.g., the MAP-9036-7 battery) shall be subjected to all applicable tests prescribed in Enclosure 2 of NAVSEANOTE 9310. All specialty Li-$(CF_x)_n$ cells and batteries which are not specifically described above shall be subjected to all applicable tests prescribed in Enclosure 2 of the referenced document.

Matsushita Electric Industrial Co., Ltd. (Panasonic Industrial Co.)
Ray-O-Vac Corporation
Union Carbide Corporation

Matsushita Electric (Panasonic) manufactures several cylindrical, button, and pin type bobbin Li-$(CF_x)_n$ cells for use in a multitude of commercial, consumer, and military applications. Both Ray-O-Vac and Union Carbide produce some of the same cell models under license from Matsushita Electric. All cells

feature a non-hermetic crimped plastic seal, an electrolyte of $LiBF_4$ in gamma-butyrolactone, and a deformable plastic top designed to open at elevated temperatures. None of the cells possess internal electrical fuses. The characteristics for each cell type are listed in the tables below. The cell model numbers used by either Ray-O-Vac or Union Carbide are identical to the model numbers designated by Matsushita. The tables also show acceptance by the UL Component Recognition and Follow-Up Service for cell models submitted by Matsushita, Ray-O-Vac, and Union Carbide.[11B]

A. Cylindrical, spirally wound cells

Cell Model Number-ANSI Size (Matsushita)	Nominal Capacity, mAh	Cell Models Offered by Ray-O-Vac	UL Component Recognition (Matsushita)	UL Component Recognition (Ray-O-Vac)	Maximum Recommended Discharge Rate, MA	Maximum Pulse A
BR-2/3AA	600		X		80	0.5
BR-1/2A	750	X	X	X	120	0.5
BR-2/3A	1200	X	X	X	250	1.0
BR-A	1800				250	1.0
BR-C	5000				300	1.0

Note: 1. All of the above cells possess negative case polarities.

2. The operational temperature range is -40 to +85°C for the cells given above.

B Pin type bobbin cells

Cell Model Number-ANSI Size (Matsushita)	Nominal Capacity, mAh	Cell Models Offered by Ray-O-Vac	UL Component Recognition (Matsushita)	UL Component Recognition (Ray-O-Vac)	Maximum Recommended Discharge Rate, mA	Maximum Pulse, mA
BR211	5.4				0.05	
BR425	25	X	X	X	0.5	4
BR435	50	X	X	X	1.0	6

Note: 1. Operational temperature range for model BR211 is -10 to +60°C; that for models BR425 is -20 to +60°C.

2. The above cells possess positive case polarities (i.e., cells are comprised of a central core of lithium.)

C. Coin/Button prismatic cells

Cell Model Number (Matsushita)	Nominal Capacity, mAh	Cell Models Offered by Ray-O-Vac and Union Carbide	UL 11B Component Recognition (Matsushita)	UL 11B Component Recognition Ray-O-Vac, Union Carbide)	Maximum Recommended Discharge Rate, Rate, mA
BR1216	25				5
BR1225	38	X	X	X	8
BR1616	45		X		8
BR2016	75	X	X	X	10
BR2020	85		X		10
BR2320	110	X	X	X	10
BR2325	165	X	X	X	10
BR2032	180		X		10
BR2330	250				10

Note: 1. The operational temperature range for all Matsushita cells listed above is -10 to +60°C. The operational temperature range for corresponding Ray-O-Vac cells is -40 to +85°C.

2. All cells listed above possess a positive case (can) polarity. The coin cell lid is the negative terminal.

Recommendations:

A. Cylindrical, spirally wound Li-$(CF_x)_n$ cells and batteries:

1. Matsushita BR-A and BR-C cells and batteries comprised of these cells shall be subjected to all applicable tests prescribed in Enclosure 2 of NAVSEANOTE 9310.
2. Matsushita BR-2/3AA, BR-1/2A, and BR-2/3A single cells as well as the Ray-O-Vac BR-1/2A and BR-2/3A single cells shall be exempt from the tests prescribed in Enclosure 2 of NAVSEANOTE 9310, with the exception of the High Temperature Test, provided a) each cell is the sole power supply for the application, b) each cell possesses an electrical fuse of an appropriately low current value (e.g., 0.10A for the 2/3AA cell, 0.15A for the 1/2A cell, and 0.30A for the 2/3A cell) located in the positive lead, and c) each cell incorporates a thermal fuse designed to interrupt the circuit at cell temperatures of 89 to 95°C. The thermal fuse shall be located as closely as possible to the cell.
3. A battery, comprised of one series-connected string of cells selected from models BR-2/3AA, BR-1/2A, and BR-2/3A, which serves as a sole power

supply for an application, shall be exempt from the tests prescribed in Enclosure 2 of NAVSEANOTE 9310, with the exception of the High Temperature Test, provided a) the required discharge current is less than 40mA, 60mA, and 125mA for batteries comprised of BR-2/3AA, BR-1/2A, and BR-2/3A cells, respectively, b) the series string of cells possesses an electrical fuse of an appropriately low current value (see 2, above) located in the negative lead, and c) a thermal fuse designed to interrupt the circuit at temperatures of 89 to 95°C is incorporated in the battery. The location of the thermal fuse shall be in the negative lead either between adjacent cells or in the geometric center of a group of series connected cells.

4. Batteries comprised of BR-2/3AA, BR-1/2A, and BR-2/3A single cells or series connected strings of these cells which are, in turn, electrically connected in parallel shall be exempt from the tests prescribed in Enclosure 2 of NAVSEANOTE 9310, with the exception of the High Temperature Test, provided a) these batteries are the sole power sources, b) each cell or series string of cells shall possess an appropriate blocking diode in the positive lead to prevent the inadvertent electrical charging of a depleted cell or series string of cells by other cells or series strings of cells, respectively, in the battery, c) the required discharge rate is less than the quantity (the number of 2/3AA, 1/2A, or 2/3A cells or series strings of these cells connected in parallel x 40mA, 60mA, or 125mA, respectively), and d) the battery shall incorporate appropriate electrical and thermal fusing, as described above, in the negative (ground) lead of the battery.

5. Cells and batteries which fulfill electrical descriptions 2 through 4, above, and also serve as support power supplies to a mains (DC) power supply shall be exempt from the tests prescribed in Enclosure 2 of NAVSEANOTE 9310, with the exception of the High Temperature Test, provided the positive lead of the cell or battery is equipped with redundant diode protection. Such protection may also be achieved through use of either an electrical fuse or a resistor located between a single diode and the mains (DC) power supply. It is important to note that the values for either the fuse or the resistor should be selected to limit any possible charging current to less than 1ma in the event of

diode failure.

B. Pin type bobbin Li-$(CF_x)_n$ cells and batteries:

Matsushita cell models BR211, BR425, and BR435, Ray-O-Vac cell models BR425 and BR435, and batteries constructed from these cells shall be exempt from all tests, with the exception of the High Temperature Test, prescribed in Enclosure 2 of NAVSEANOTE 9310. It is important to note that the maximum lithium content in the largest cell (BR435, 50mAh capacity) is only about 0.015 gram. The High Temperature Test should be modified to account for the small size and pencil shape of these cells.

C. Coin/button prismatic Li-$(CF_x)_n$ cells and batteries:

All button cells (and batteries comprised of these cells) manufactured by Matsushita, Ray-O-Vac, and Union Carbide shall be exempt from the tests prescribed in Enclosure 2 of NAVSEANOTE 9310, with the exception of the High Temperature Test. The High Temperature Test should be modified to more accurately determine the worst case hazards for these small cells and batteries. Batteries shall be required to possess all appropriate electrical and thermal protective devices such as those previously discussed for batteries comprised of cylindrical Li-$(CF_x)_n$ cells.

Manufacturers: Eagle-Picher Industries
Matsushita Electric Industrial Co., Ltd.
(Panasonic Industrial Co.)
Ray-O-Vac Corporation
Union Carbide Corporation

Toxicity:

1. Polycarbon monofluoride, $(CF_x)_n$, will decompose at temperatures of 350°C or higher to yield highly toxic fluoride fumes.
2. Eagle-Picher cells contain a solution of $LiAsF_6$ in dimethyl sulfite, $(CH_3)_2SO_3$, as the electrolyte. Both components should be considered as potentially toxic materials. Dimethyl sulfite will emit highly toxic SO_x fumes upon decomposition at elevated temperatures.
3. Matsushita (Panasonic), Ray-O-Vac, and Union Carbide cells contain a solution of $LiBF_4$ in gamma-butyrolactone as the electrolyte. The specific toxicity of both components is not known at this time.

4. Lithium fluoride, LiF, as well as other lithium salts (e.g., $LiBF_4$ and $LiAsF_6$) pose a general toxicity hazard to the Central Nervous System (CNS) when ingested.

Flammability: Gamma-butyrolactone is a slight fire hazard.

Lithium-Sulfur Dioxide[33-52] Li-SO_2

All lithium-sulfur dioxide batteries procured in accordance with MIL-B-49430(ER) with its three Amendments[53] and which have passed contractually required testing and U.S. Army sample testing shall be exempt from the test procedures prescribed in Enclosure 2 of NAVSEANOTE 9310 with the exception of the High Temperature Test. Specifically, only U.S. Army batteries designated BA-5567/U, BA-5847/U, BA-5599/U, BA-5600/U, BA-5588/U, BA-5598/U, BA-5513/U, BA-5557/U, and BA-5590/U meet the above qualifications. A tenth battery, BA-5093/U shall be included in the above listing pending U.S. Army approval.

<u>Restrictions</u>:

1. THE ABOVE BATTERIES SHALL NOT BE USED IN APPLICATIONS WHICH REQUIRE DISCHARGE PROFILES ABOVE THE OPERATIONAL DESIGN LIMITS AS SPECIFIED IN MIL-B-49430(ER).
2. NO OTHER Li-SO_2 CELLS OR BATTERIES OF EITHER THE ELECTROCHEMICALLY BALANCED OR UNBALANCED DESIGNS SHALL BE EXEMPT FROM THE TESTS PRESCRIBED IN ENCLOSURE 2 OF NAVSEANOTE 9310. RESERVE Li-SO_2 BATTERIES SHALL BE TESTED IN ACCORDANCE WITH PROCEDURES TO BE GIVEN IN NAVSEAINST 9310.1B.
3. Total containment of all cell contents is mandatory for battery use aboard submarines, in aircraft cockpits, and in such critical applications as air mask systems having Li-SO_2 batteries as power supplies for the blower motor.
4. The use of the BA-5567/U is restricted to applications using this single cell as the sole power source. This unit does not possess fusing or diode protection.
5. The Military Specification Sheet for the BA-5600/U battery, MIL-B-49430/8A(ER) of 4 January, 1985, specifies a 2.25A non-replaceable time delay fuse in the <u>positive</u> leg. This fuse placement must be taken into account at the Safety Design Review in the event that an end item containing the BA-5600/U battery is proposed for a U.S. Navy application.

Lithium-Sulfur Dioxide
Li-SO_2
(cont.)

Li-SO_2 Manufacturers: Duracell International
Honeywell (custom cells/batteries)
Power Conversion Inc.
SAFT
TNR

Toxicity: Sulfur dioxide (SO_2) is highly toxic. Concentrations of 500 ppm are considered to be immediately dangerous to life while concentrations of 50 to 100 ppm are the maximum permissible concentration levels for exposure of 30 to 60 minutes. Sulfur dioxide reacts with moist air to form sulfurous acid, H_2SO_3, which slowly converts to sulfuric acid, H_2SO_4.

Flammability: Acetonitrile (CH_3CN) is flammable when exposed to heat, flame, or oxidizers. When heated to decomposition, acetonitrile will emit highly toxic cyanides.

Lithium-Sulfuryl Chloride Systems[54-58]
$Li-SO_2Cl_2$ and $Li-Cl_2$ in SO_2Cl_2

Only the lithium-chlorine in sulfuryl chloride ($Li-Cl_2$ in SO_2Cl_2) system is produced commercially at this time. Electrochem Industries, a division of Wilson Greatbatch, Ltd., manufactures three types of $Li-Cl_2$ in SO_2Cl_2 cells: a) the CSC series of cells for high drain rates (0.5 A, D cell), b) the PWR series of cells for higher drain rates (2.0 A, D cell), and c) the RMM series of cells for applications at temperatures up to 150°C. The cell sizes for each type are given below:

Size	CSC	PWR	RMM
1/2 AA	X		
2/3 A	X		
AA	X		
2/5 C	X		
1/2 C	X	X	
C	X		X
D	X	X	X
DD	X	X	

Of all the cells listed above, only the PWR DD size cell used in the U.S. Navy EMATT program is provided with a reliable vent structure at this time. The normal venting mechanism for the CSC and PWR cells depends upon the fracture of the glass to metal seal. The RMM C and D cells are designed to withstand very high internal pressures at temperatures up to 150°C. As a result, explosions may occur for these cells subjected to both thermal and electrical abuse conditions.

Recommendations: $Li-Cl_2$ in SO_2Cl_2 cells and batteries of the CSC, PWR, and RMM types shall be tested in accordance with the tests prescribed in Enclosure 2 of NAVSEANOTE 9310.

Manufacturer: Electrochem Industries, a division of Wilson Greatbatch Ltd.

Toxicity: SO_2Cl_2 forms HCl and H_2SO_4 when exposed to moist air, highly toxic

Flammability: none

Lithium-Thionyl Chloride Based Systems[59-72]
Li-$SOCl_2$ and Li-BrCl in $SOCl_2$

Lithium-thionyl chloride (Li-$SOCl_2$) cells and batteries are currently available from several manufacturers for use in commercial, military, and medical applications. Electrochem Industries produces Li-$SOCl_2$ cells which incorporate the interhalogen, BrCl, as a second cathode component. Both cell systems offer higher cell load voltages and greater gravimetric and volumetric energy densities than most other lithium electrochemical systems. Nominal capacities for cells vary from about 0.1Ah for the miniature bobbin or button cells to 10,000Ah for the large GTE prismatic cells used as power supply support for the Minuteman ICBM.

Perhaps the most serious safety-related deficiency for many lithium-thionyl chloride based systems is the inability to successfully develop and incorporate safe, reliable mechanical vent structures in cells to relieve the internal pressures resulting from abusive conditions. Venting of highly toxic $SOCl_2$ or BrCl in $SOCl_2$[6] is the more acceptable alternative to cell rupture or explosion. Indeed, the U.S. Army Specification, MIL-B-49461(ER) requires all Li-$SOCl_2$ cells in batteries to vent through designed structures at temperatures between 196°F (91°C) and a maximum of 320°F (160°C).[73] The presence of a reliable vent structure in the Li-$SOCl_2$ cells assessed in this study is a major consideration in determining whether such cells shall be exempt from some or all of the tests given in Enclosure 2 of NAVSEANOTE 9310. Other factors include: lithium content, surface area/internal design (e.g., spirally wound, prismatic, or bobbin structures), safety features, and demonstrated tolerance to abusive conditions.

Altus Corporation

Altus Corporation manufactures cylindrical and disc $Li\text{-}SOCl_2$ cells for use in medium to high rate military and commercial applications. These cells feature ceramic-to-metal hermetic seals, case positive polarity, and an operational temperature range of -40 to +70°C. Under extreme abuse conditions, cell venting is expected to occur through the ceramic seal. All Altus cells possess a patented "electrochemical switch" designed to shunt up to 70% of the current through a cell in voltage reversal. It is important to note that the current shunt is effective during forced overdischarge at current levels equal to or less than the nominal discharge rate for each specific cell. The characteristics for the cylindrical and disc cells are given below:

I. Cylindrical, Spirally Wound Cells

Model Number	ANSI Size	Nominal Capacity, Ah	Maximum Recommended Discharge Rate, A
AL½AA	½AA	0.66	0.3
AL2-AA	AA	2.0	1.5
AL6-C	C	6.0	1.0
AL14-D	D	14	10
AL18-F	F	18	10

NOTE: 1. All of the above cells possess internal electrical fuses.

2. None of the above cells are accepted as recognized components by Underwriters Laboratories.

II. Disc Cells, Prismatic Internal Design

Model Number	Dimensions Diameter, cm x Thickness, cm	Nominal Capacity, Ah	Maximum Recommended Discharge Rate, A
AL125	3.23 x 0.97	1.4	0.3
AL250	6.35 x 1.02	5.5	1.0
AL400	10.2 x 1.17	15	2.9

NOTE: 1. None of the above disc cells possess internal electrical fuses.

2. All of the above cells are accepted by the Underwriters Laboratories' Component Recognition and Follow-Up Service.[11D]

Recommendations: All of the above cells and batteries comprised of these cells shall be subjected to all applicable tests prescribed in Enclosure 2 of

NAVSEANOTE 9310.

Altus also produces a 7.3V, 1.7Ah battery (model AL9V) comprised of two Li-$SOCl_2$ cells in series. The component cell does not appear to be one of those cells listed above. The battery is dimensionally similar to the NEDA 1604 battery envelope (i.e., 4.83 cm high x 2.59 cm wide x 1.63 cm thick). The operational temperature is -20 to +70°C. The battery is designed to operate at a current level of about 25mA to a maximum recommended discharge rate of about 0.5A. An internal electrical fuse is incorporated into the battery circuit.

Recommendation: The AL9V battery shall be exempt from the Short Circuit Test prescribed in Enclosure 2 of NAVSEANOTE 9310. All other applicable tests shall be conducted.

Altus manufactures several specialty Li-$SOCl_2$ active cells for the U.S. military. These cells are typically of the disc design with internal prismatic construction. Examples include the HI-G cell/battery designed to resist vigorous dynamic spin and shock environments and the High Energy Density Battery (HEDB) comprised of 1400 or 2000Ah disc cells. The HEDB batteries were developed for U.S. Navy applications.

Recommendation: The above cells and batteries comprised of these cells shall be subjected to all applicable tests prescribed in Enclosure 2 of NAVSEANOTE 9310.

In addition to manufacturing active Li-$SOCl_2$ cells and batteries, Altus also produces several Li-$SOCl_2$ reserve batteries for military applications requiring high pulse power levels.

Recommendation: All reserve batteries shall be subjected to the tests prescribed in NAVSEAINST 9310.1B. The Expendable Reliable Acoustic Path Sonobuoy (ERAPS) battery shall be subjected either to the appropriately modified test program prescribed in the Naval Avionics Center (NAC) document SPD-10 or to the specific test program prescribed in NAVSEAINST 9310.1B.

Eagle-Picher Industries, Inc.

The Electronics Division of Eagle-Picher produces KEEPER II lithium-thionyl chloride ($Li-SOCl_2$) cells and batteries which are specifically designed as power supplies for Complementary Metal Oxide Semiconductor (CMOS) memory back-up applications. The basic, non-standard cells feature internal prismatic construction, a glass-to-metal seal, and wider ranges of operational temperatures than most $Li-SOCl_2$ cells. Cells and batteries possess neither electrical and thermal safety devices nor a venting mechanism. Glass-to-metal seal failure is intended to serve as the only means to relieve the high internal pressures attendant with thermal abuse conditions. Except for cell models LTC-30P and LTC-120P, all cells and batteries listed below have been accepted by the Underwriters Laboratories (UL) Component Recognition and Follow-Up Service:[11D]

A. Cells:

Model Number	Height, cm	Width, cm	Thickness, cm	Nominal Capacity, Ah	Maximum Recommended Discharge Rate, mA
LTC-7PN	2.54	1.65	0.64	0.75	50
LTC-7P	3.05	1.78	0.84	0.75	50
LTC-12P	2.54	1.35	1.35	1.2	30
LTC-16P	3.66	1.35	1.35	1.6	40
LTC-20P	4.92	1.35	1.35	1.6	50
LTC-30P	4.92	1.35	1.35	2.6	50
LTC-120P	5.1	14.0	5.21	12	200

Note: 1. The operational temperature range for cell models LTC-7PN and LTC-7P is -40 to +125°C while that for all other cell models is -40 to +93°C.

2. Model LTC-7PN is the basic component cell for model LTC-7P (a LTC-7PN cell potted into a plastic cover jacket) and battery models LTC-7PMS and LTC-7PMP.

B. Batteries:

Model Number	Height, cm	Width, cm	Thickness, cm	OCV, V	Nominal Capacity, Ah	Maximum Recommended Discharge Rate, mA
LTC-7PMS	3.81	3.05	0.84	7.3	0.75	50
LTC-7PMP	3.81	3.05	0.84	3.65	1.5	100
LTC-16P9	4.57	2.86	1.75	7.3	1.6	40

NOTE: 1. Model number LTC-7PMS is comprised of two LTC-7PN cells connected in series. Model number LTC-7PMP is comprised of two LTC-7PN cells connected in parallel. Both batteries are potted into plastic cover jackets. The operational temperature range for these batteries is -40 to +125°C.

2. Model number LTC-16P9 is comprised of two LTC-16P cells connected in series. This battery design conforms to the configurational specifications for a NEDA L1604 battery. The operational temperature range is -40 to +93°C.

Recommendation:

1. Model LTC-30P and LTC-120P cells and batteries constructed from these cells shall be subjected to all applicable tests as prescribed in Enclosure 2 of NAVSEANOTE 9310.
2. Model LTC-7PN through LTC-20P single cells shall be exempt from the tests prescribed in Enclosure 2 of NAVSEANOTE 9310, with the exception of the High Temperature Test, provided a) each cell is the sole power supply for the application, b) each cell possesses an electrical fuse of low current value (e.g., 0.1A) located in the positive lead, and c) each cell incorporates a thermal fuse designed to interrupt the circuit at temperatures of 89 to 95°C. The thermal fuse shall be located as closely as possible to the cell.
3. A single series-connected string of cells selected from models LTC-7PN through LTC-20P which serves as a sole power supply shall be exempt from the tests prescribed in Enclosure 2 of NAVSEANOTE 9310, with the exception of the High Temperature Test, provided a) the required discharge current is less than five (5) mA, b) the series string of cells possesses an electrical fuse of low current value (e.g., 0.1A) located in the negative lead, and c) the series string of cells incorporates a thermal fuse designed to interrupt the circuit at temperatures of 89 to 95°C. The location of the thermal fuse shall be in the negative lead either between adjacent cells or in the geometric center of a group of series-connected cells.
4. Batteries comprised of cells or series strings of cells (from Models LTC-7PN through LTC-20P) which are, in turn, electrically connected in

parallel shall be exempt from the tests prescribed in Enclosure 2 of NAVSEANOTE 9310, with the exception of the High Temperature Test, provided a) these batteries are sole power sources, b) the required discharge rate is less than the quantity (5mA x number of cells or series strings of cells connected in parallel), c) each cell or series string of cells shall incorporate an appropriate blocking diode in the positive lead to prevent the inadvertent electrical charging of a depleted cell or series string of cells by other cells or series strings of cells, respectively, in the battery, and d) the battery shall incorporate the appropriate electrical and thermal fusing, as described above, in the negative (ground) lead of the battery.

5. Cells and batteries which fulfill the descriptions of 2 through 4, above, and which serve as back-up power supplies to a mains (DC) power supply shall be exempt from the tests prescribed in Enclosure 2 of NAVSEANOTE 9310, with the exception of the High Temperature Test, provided the positive lead of the cell or battery is equipped with redundant diode protection. Such protection may also be achieved through use of either an electrical fuse or a resistor located between a single diode and the mains (DC) power supply. It is important to note that the values for either the fuse or the resistor should be selected to limit any possible charging current to less than 5mA in the event of diode failure.

Eagle-Picher also manufactures customized $Li-SOCl_2$ reserve batteries for use in several U.S. military programs requiring standby power. An Eagle-Picher reserve battery was recently selected as the power supply for the Acoustic Device Countermeasure Vehicle EX9 (ADCV EX9) program in the U.S. Navy. Such reserve batteries shall be subjected to the specialized test program given in NAVSEAINST 9310.1B.

Electrochem Industries (A Division of Wilson Greatbatch Ltd.)

Electrochem Industries (E I) currently manufactures several ANSI standard sized Li-BrCl in $SOCl_2$ (Li-BCX) cylindrical cells. These cells feature a spirally-wound internal design, a glass-to-metal hermetic seal, and electrical fuses or fuse links incorporated into the area beneath the terminal cap. There is no venting mechanism other than the glass-to-metal seal. Model 3B50 (Printed Circuit, (PC) cell) is a coin cell having a prismatic internal design. Its major application is as a back-up power supply for Complementary Metal Oxide Semiconductor (CMOS) memory. The 3B50 cell possesses neither an electrical fuse nor a venting mechanism. Models 3B27(AA), 3B64(AA), 3B39(AA), 3B50(PC), and 3B70(C) cells have been accepted by the Underwriters Laboratory (UL) Component Recognition and Follow-Up Service.[11D] The characteristics for Li-BCX cells are given below:

Model Number	ANSI Size	Nominal Capacity, Ah	Maximum Recommended Discharge Rate, mA	Internal Fusing Value*, A
3B26	½AA	0.8	20	4 FL
3B27	AA	1.5	100	4 FL
3B64	AA	2.0	100	4 FL
3B39	AA	2.0	100	4 FL
3B50	---	1.0	11	NONE
3B793	2/3AA	2.0	20	1 F
3B70	C	7.0	500	4 F
3B75	D	14.0	1000	4 F
3B76	DD	30.0	3000	4 F

* FL = fuse link, a notched section in an internal lead
F = miniature electrical fuse

Notes:

1. Cell model 3B27(AA) contains 0.5g or less of Li in order to comply with 49 CFR 173.206f, DOT transportation regulations (Half Gram Rule).
2. Cell model 3B39 is the same basic cell as model 3B64 except that the labeling is etched onto the stainless steel cell case.
3. Cell model 3B50 is a coin cell having a diameter of 2.53cm and height of 0.75cm.
4. Cell models 3B26, 3B27, 3B64, 3B39, and 3B50 possess positive case polarities; all other cell models possess negative case polarities.

Recommendations: All Li-BrCl in $SOCl_2$ cells and batteries comprised of these cells shall be subjected to all applicable tests prescribed in Enclosure 2 of NAVSEANOTE 9310.

GTE Strategic Power Systems Division

GTE produces both standard cylindrical and large prismatic Li-$SOCl_2$ cells for use in several commercial and military applications. All cylindrical cells feature glass-to-metal hermetic seals, and the low rate bobbin internal construction. No venting device or internal electrical fuse are present in these bobbin cells. The characteristics for these cells are given below:

Model Number	ANSI Size	Nominal Capacity, Ah	Maximum Recommended Discharge Rate, mA
LAA/2-1	½AA	0.7	3
LAA-1	AA	1.8	20
LC-1	C	5.5	60
LC-3HT	C	5.5	60
LD-2	D	10	100
LDD-3HT	DD	23	200
LDD-1	DD	27	200

NOTE: 1. Models LC-3HT and LDD-3HT cells are designed for operation at temperatures of -40 to +150°C. The operating temperature range for all other cells is -40 to +50°C.

Recommendation: Little safety-related data are available for the cell models given above. However, some low capacity cells (models LAA/2-1, LAA-1, and LC-1) and batteries comprised of these cells shall only be exempt from the Short Circuit Test prescribed in Enclosure 2 of NAVSEANOTE 9310. Cells and batteries of the specific models LC-3HT (C), LD-2 (D), LDD-3HT (DD), and LDD-1 (DD) shall be subjected to the Short Circuit Test. All other applicable tests prescribed in Enclosure 2 of NAVSEANOTE 9310 shall be conducted.

The large prismatic cells manufactured by GTE are exclusively used in military applications requiring reliable standby power. Each cell features a resealable vent device located in the cell top. These cells are designed for low rate (e.g., 250 hour discharge) applications. The characteristics for three cell types are given below:

Model Number	Nominal Capacity, Ah	Normal Discharge Rate, A	Maximum Recommended Discharge Rate, A
LP-020	2000	8	16
LP-045	4500	18	36
LP-100	10,000	40	80

NOTE: 1. None of the cells listed above possess internal electrical fuses.

2. The operational temperature range for the above cells is -40 to +50°C.

Recommendation: The prismatic cells, LP-020, LP-045, and LP-100, shall be exempt from the Short Circuit Test prescribed in Enclosure 2 of NAVSEANOTE 9310. Batteries comprised of the three cell models, however, shall be subjected to the Short Circuit Test. All other applicable tests prescribed in Enclosure 2 of NAVSEANOTE 9310 shall be conducted upon both the single cells and batteries.

GTE Strategic Power Systems Division also specializes in the design and fabrication of $Li\text{-}SOCl_2$ reserve battery systems for military applications. All production units submitted to the U.S. Navy shall be subjected to the safety test program for reserve battery systems given in NAVSEAINST 9310.1B.

Hellesens Battery Engineering, Inc., Battery Engineering, Inc., A/S Hellesens (Søborg, Denmark)

Hellesens Battery Engineering, Inc. (Battery Engineering, Inc.) of Hyde Park, MA. manufactures three basic Li-$SOCl_2$ cell types for use in the U.S. military and in such diverse commercial applications as Complementary Metal Oxide Semiconductor (CMOS) memory back-up, medically implantable devices, wildlife telemetry, and oil well monitoring systems. Each of the three cell types are discussed below:

A. Low Rate Cells: Except for Model 23-3H (button design), these cylindrical cells feature an internal bobbin construction, a glass-to-metal hermetic seal, and a negative case polarity. Neither a venting mechanism nor an internal electrical fuse are included in the design of these cells. Except as noted below, the operational temperature range for the cells is -40 to +70°C. The characteristics for the cells are given below:

Model Number	Diameter, cm	Height, cm	ANSI Size	Nominal Capacity, Ah	Maximum Recommended Discharge Rate, mA
10-10	1.0	1.3	---	0.10	0.5
10-12	1.0	1.5	---	0.14	0.5
10-18	1.0	2.1	---	0.30	1.0
10-25	1.0	2.8	---	0.48	1.0
10-35	1.0	3.8	---	0.75	1.5
10.42	1.0	4.5	AAA	0.90	2.0
10-54	1.0	5.7	---	1.2	3.0
13-38	1.3	4.1	---	1.3	5.0
14-24	1.4	2.7	½AA	0.85	4.0
14-48	1.4	5.1	AA	1.8	10
23-3H	2.4	0.35	Button	0.3	3.0
26-48	2.6	5.0	C	4.5	30
26-101	2.6	10.3	CC	16	0.5
33-60	3.3	6.2	D	11	60
33-127	3.3	12.9	DD	28	100

Note:

Model(s)	Maximum Operating Temperature, °C
10-18 and 10-35	100
26-48 and 33-60	135
33-127	140

Recommendation: Little safety-related data are available for the cell models given above. Nonetheless, most cells or batteries comprised of these cells shall be exempt from the Short Circuit Test prescribed in Enclosure 2 of NAVSEANOTE

9310. Cells and batteries of Models 26-48 (C), 26-101 (CC), 33-60 (D), and 33-127 (DD) shall be subjected to the Short Circuit Test. All other applicable tests prescribed in Enclosure 2 of NAVSEANOTE 9310 shall be performed.

B. High Rate Cells: These cylindrical cells feature a spirally-wound cell design, a glass-to-metal hermetic seal, negative case polarity, and a vent mechanism consisting of a puncturable plastic diaphragm. The operational temperature range is -40 to +70°C. These cells do not possess electrical fuses within the cell structure. The characteristics for these cells are given below:

Model Number	Diameter, cm	Height, cm	ANSI Size	Nominal Capacity, Ah	Maximum Recommended Discharge Rate, A
26-48H	2.6	5.0	C	4.5	0.2
33-60H	3.3	6.2	D	10.7	0.5
33-127H	3.3	12.9	DD	26	1.0

Recommendation: The above high rate cells and batteries comprised of such cells shall be subjected to all applicable tests prescribed in Enclosure 2 of NAVSEANOTE 9310.

C. High Temperature Cells: These cells are designed to operate at temperatures up to a maximum of +150°C. The high temperature cells feature internal bobbin construction, a glass-to-metal hermetic seal, and negative case polarity. No vent mechanism or electrical fuses are included in this design. The characteristics for these cells are given below:

Model Number	Diameter, cm	Height cm	ANSI Size	Nominal Capacity, Ah	Maximum Recommended Discharge Rate, mA
14-50HT	1.4	5.1	AA	1.8	10
26-48HT	2.6	5.0	C	6.2	60

Recommendation: Cells and batteries of the high temperature design shall be subjected to all applicable test prescribed in Enclosure 2 of NAVSEANOTE 9310.

Hellesens Battery Engineering/Battery Engineering also specializes in the design of reserve battery systems comprised of either conventional or bipolar cells. Any production units submitted for U.S. Navy applications shall be subjected to the safety test program given in NAVSEAINST 9310.1B.

A/S Hellesens of Søborg, Denmark markets ANSI C and 6 size cells and batteries in the United States through either Hellesens Battery Engineering/Battery Engineering or M.H. Johnson of Verona, WI. Both cell types are of the low rate bobbin construction design and feature glass-to-metal hermetic seals. Each cell possesses a reverse biased diode in parallel for at least some protection against cell voltage reversal and a polymeric positive temperature coefficient (PTC) resistor for protection against high current discharge and/or high temperature operation. There exists no vent mechanism other than the glass-to-metal seal in either cell type. Performance is dependent upon cell orientation. The operational temperature range for cells and batteries is -40 to +70°C. The characteristics for the two cell types are given below:

Model Number	Diameter, cm	Height, cm	ANSI Size	Nominal Capacity, Ah	Maximum Recommended Discharge Rate, A
HE251	2.7	5.4	C	5.0	0.1
HE255	6.7	16.5	6	125	1.0

Recommendation: Explosions have occurred when cells are thermally abused under incineration or localized heating conditions. Testing of these cells in strict accordance (i.e., all electrical safety devices bypassed) with all applicable test requirements prescribed in Enclosure 2 of NAVSEANOTE 9310 is recommended.

A/S Hellesens also produces a standard line of batteries using the above cells as the components:

A. Batteries comprised of one series-connected string of cells possess, in addition to the safety devices incorporated with each component cell, a series connected blocking diode to prevent the inadvertent charging of the battery by a mains power supply. These batteries do not incorporate an electrical fuse in the circuit. The characteristics for these batteries are summarized below:

Battery Number	Component Cell (ANSI)	Number of Cells Connected in Series	OCV, V	Nominal Capacity, Ah	Maximum Recommended Discharge Rate, A
HE294*	C	2	7.2	6	0.1
HE250*	C	2	7.2	6	0.1
HE265*	6	4	14.4	125	1.0
HE260*	6	4	14.4	125	1.0
HE267	6	5	18.0	125	1.0
HE274	6	7	25.2	125	1.0

* Component cells in batteries:

a) HE294 and HE265 are arranged in a cell stack.
b) HE250 are arranged side-by-side.
c) HE260 are arranged in a square.

Recommendation: The above batteries shall be subjected to all applicable tests prescribed in Enclosure 2 of NAVSEANOTE 9310.

B. Batteries comprised of ANSI number 6 cells or series strings of ANSI number 6 cells which are electrically connected in parallel possess, in addition to the safety devices incorporated with each component cell, a 10A electrical fuse and, with the one exception as noted, a series-connected blocking diode to prevent the inadvertent charging of the battery by a mains power supply. Hellesens also suggests inclusion of blocking diodes on each series string to prevent the charging of a depleted series string of cells by one or more other series strings in the battery. The characteristics for these batteries are given below:

Battery Number	Number of Cells Connected in Series	Number of Cells or Series Strings Connected in Parallel	OCV, V	Nominal Capacity, Ah	Maximum Recommended Discharge Rate, A
HE254*	(1)	7	3.6	875	2.5
HE261	2	2	7.2	250	2.0
HE258	4	3	14.4	375	2.5
HE259	4	7	14.4	875	2.5
HE266	5	3	18.0	375	2.5
HE257	5	5	18.0	625	2.5

* HE254 does not possess a series-connected diode.

Recommendation: The above batteries consisting of electrically connected cells or strings of cells in a parallel arrangement shall be subjected to all tests prescribed in Enclosure 2 of NAVSEANOTE 9310.

Honeywell Corporation, Power Sources Center

Honeywell does not offer a standard line of Li-$SOCl_2$ cells or batteries for commercial and military applications. Rather, highly specialized cells and batteries have been developed by Honeywell for exclusive use in the aerospace and military environment. Large, active cells of prismatic design which range in capacities from 165 Ah to 16,500 Ah have been designed and tested for the U.S. Air Force.

Recommendation: All cells and batteries comprised of the cells described above which are submitted to the U.S. Navy shall be subjected to all applicable tests prescribed in Enclosure 2 of NAVSEANOTE 9310.

Honeywell also specializes in the design and fabrication of Li-$SOCl_2$ reserve battery systems comprised of either the conventional or the bipolar cell construction.

Recommendation: Any production end units containing reserve Li-$SOCl_2$ batteries are to be subjected to the reserve battery safety test program prescribed in NAVSEAINST 9310.1B.

Power Conversion, Inc.

Power Conversion, Inc. (PCI) manufactures several sizes of low rate lithium-thionyl chloride ($Li-SOCl_2$) cylindrical cells specifically designed for Complementary Metal Oxide Semiconductor (CMOS) memory support as well as other standby power applications. All PCI cells feature a modified bobbin internal design consisting of one to four layers (dependent upon cell size) of a wound lithium anode strip pressed against the inner circumference of the cell case (case negative polarity). The carbon electrode cylinder consists of a similarly wound strip of carbon electrode which occupies the cell center. These cells possess glass-to-metal hermetic seals and coined vent mechanisms to relieve high internal pressures attendant with electrical and thermal abuse conditions. The vents are designed to open at the pressures generated when internal cell temperatures exceed 150°C. The normal operational temperature range for all cells is -40 to +74°C. None of the cells possess internal electrical fuses. However, PCI does recommend the incorporation of a time delay fuse in board circuits. In addition, PCI requires a series diode or a series diode/resistor combination for cells connected in parallel with a mains DC power supply. PCI recommends inclusion of blocking diodes in the positive leads of cells or series strings of cells electrically connected in parallel. It is important to note that the maximum recommended discharge current for all cells or series string of cells is equivalent to the one thousand hour rate. A summary of the characteristics for all active $Li-SOCl_2$ cells manufactured by PCI is given below:

Model Number	ANSI Size	Nominal Capacity, Ah	Maximum Recommended Discharge Rate, mA
T04	½AA	0.8	0.8
T06	AA	1.7	1.7
T31	½A	0.9	0.9
T32	2/3A	1.4	1.4
T52	C	5.0	5.0
T20	D	10	10

NOTES: 1. Models T31 and T32 are listed as ½AA and 2/3AA sized cells, respectively, in PCI sales brochures. The diameter for each of the two cell models, however, corresponds to the ANSI A-sized cell.

2. The ½AA and D cells possess coined vents on the walls of the cell cylinder; all other cell sizes possess coined vents on the bottom

face of the cylinder (i.e., opposite end from the glass-to-metal hermetic seal).

3. All cell sizes, with the exception of the ½A cell (model T31) have been accepted by the UL Component Recognition and Follow-Up Service.[11D]

4. UL observed electrolyte leakage in some cells exposed a) to longterm storage and discharge conditions at 71°C and b) to forced overdischarge and charge conditions. All cells subjected to the UL heating test vented prior to attaining the final temperature of 180°C.

Recommendations:

1. Total containment of all cell contents is mandatory for cell or battery use in such critical applications as those encountered aboard submarines or in aircraft cockpits. The content of highly toxic $SOCl_2$ in fresh cells varies from about 3 grams in the ½AA size cell to about 35 grams in the D size cell.

2. The single cells of ½AA (T04), AA(T06), ½A (T31), 2/3A (T32), C (T52), and D (T20) and batteries comprised of the ½AA (T04), AA(T06), ½A (T31), and 2/3A (T32) cells shall be exempt from the testing prescribed in Enclosure 2 of NAVSEANOTE 9310, with the exception of the High Temperature Test, provided that the General condition and the applicable Specific condition(s) given below are met:

   a) General condition: 1) The operational temperature shall be 70°C or less, and 2) The discharge rate for a cell, or series string of cells, shall be no greater than that current level corresponding to the 1000 hour discharge rate.

   b) Specific conditions:

      1) A cell or single series string of cells used as the sole source of power shall incorporate an appropriate, low current value electrical fuse in the negative (ground) lead.

      2) A single series string of cells used as a sole source of power shall, in addition to 1), above, incorporate a thermal fuse designed to interrupt the circuit at temperatures of 89 to 95°C.

This fuse shall be located between adjacent cells or in the geometric center of a group of cells.

3) Batteries to be used as sole power sources, comprised of cells or series connected string of cells which are electrically connected in parallel, shall incorporate blocking diodes in the positive leads of each cell or series connected string of cells, respectively. Appropriate electrical and thermal fusing shall also be required for these batteries.

4) Cells and batteries which serve as back-up power supplies to a DC mains power supply shall, in addition to the applicable electrical and thermal safety features (above), be equipped with redundant diode protection located in the positive lead. Such protection may also be achieved through use of either an electrical fuse or a resistor located between a single diode and the mains (DC) power supply. It is important to note that the values for either the fuse or the resistor should be selected to limit any possible charging current to less than 10mA in the event of diode failure.

3. Batteries comprised of C cells (T52) and D cells (T20) shall be subjected to all applicable tests prescribed in Enclosure 2 of NAVSEANOTE 9310.

SAFT America, Inc.

SAFT manufactures cylindrical $Li\text{-}SOCl_2$ cells for use in applications requiring medium to high current levels. All cells feature glass-to-metal hermetic seals and can operate in the temperature range of -40°C to +70°C. The characteristics for these cells are given below:

Model Number	ANSI Size	Nominal Capacity, Ah	Maximum Recommended Discharge Rate, mA
LS-3	½AA	1.0	5 (100 pulse)
LS-120	AAA	1.1	10
LS-6	AA	1.7	5 (25 pulse)
LSH-20	D	10	2000 (10,000 pulse)

NOTE:
1. Models LS-3, LS-120, and LS-6 are accepted by the Underwriters Laboratories' Component Recognition and Follow-Up Service.
2. Models LSH-20 and LS-6 have case negative polarity; LS-3 and LS-120 are case positive polarity.
3. The D cell, LSH-20, possesses a spirally wound internal construction and an internal electrical fuse.
4. Models LS-3, LS-120, and LS-6 possess a bobbin internal construction. Cell model LS-6 has a coined vent in the cell bottom. No other cells listed above have mechanical vents.

SAFT also produces a 1.7Ah NEDA L1604 battery (model LS-622) comprised of two LS-120 cells connected in series. The normal operating temperature range for the battery is -40 to +70°C. This battery may be discharged at rates as high as 50mA.

Recommendation: All cells and batteries comprised of the cells listed above shall be subjected to all applicable tests as prescribed in Enclosure 2 of NAVSEANOTE 9310.

Tadiran Israel Electronics Industries, Ltd.

Tadiran manufactures several low rate cylindrical cells for both commercial and military applications. In general, these cells possess internal bobbin construction with lithium swaged onto the inside wall of the case. None of the cells have either internal fuses or means for venting, except where noted. The operational temperature range for all cells produced by Tadiran is -55 to +75°C. The characteristics for the Tadiran standard cylindrical cells are given below:

Model Number	ANSI Size	Nominal Capacity, Ah	Maximum Recommended Discharge Rate, mA
TL-2150	½AA	0.85	15
TL-2150/X	½AA	0.85	15
TL-2100	AA	1.75	42
TL-2100/X	AA	1.75	42
TL-2200	C	5.2	90
TL-2300	D	10.5	135
TL-5137	DD	20.0	250

NOTE: 1. All of the above cell models, with the exception of TL-5137 (DD cell) have been accepted by the Underwriters Laboratories (UL) Component Recognition and Follow-Up Service.[11D]

2. Those model numbers ending in X possess venting mechanisms.

Recommendation:

1. The above cells, with the exception of the DD cell, model TL-5137, shall be exempt from the Short Circuit Test prescribed in Enclosure 2 of NAVSEANOTE 9310.
2. The model TL-5137 cell, batteries comprised of the TL-5137 cell, and batteries comprised of all other cell models given above shall be subjected to all the applicable tests prescribed in Enclosure 2 of NAVSEANOTE 9310.

The cylindrical cells listed below are available by special order only:

Model Number	ANSI Size	Nominal Capacity, Ah	Maximum Recommended Discharge Rate, mA
TL-5133	1/3D	3.7	42
TL-5121	1/3C	2.0	30

Notes: 1. Neither of the two cell models have been accepted into the UL Component Recognition and Follow-Up Service.

2. The major application of these cells is as a back-up power supply for Complementary Metal Oxide Semiconductor (CMOS) memory.

Recommendation:

1. The above cell models, TL-5133 and TL-5121, shall be exempt only from the Short Circuit Test prescribed in Enclosure 2 of NAVSEANOTE 9310. All other applicable tests shall be conducted.

Tadiran also produces several cylindrical cells specifically designed for such very low rate applications as those required for CMOS memory back-up. All cell models given below have been accepted into the UL Component Recognition and Follow-Up Service:

Model Number	ANSI Size	Nominal Capacity, Ah	Maximum Recommended Discharge Rate, mA
TL-5186	*	0.30	1.0
TL-5101	½AA	0.85	0.5
TL-5101/X	½AA	0.85	0.5
TL-5134	*	1.0	3.0
TL-5104	AA	2.0	1.5
TL-5104/X	AA	2.0	1.5
TL-5105	C	5.3	3.0
TL-5106	D	10.8	4.5
TL-5135	1/6D	1.0	0.7

* Dimensions for the Tl-5186 cell are 2.05cm diameter by 0.65cm high; dimensions for the TL-5134 cell are 3.29cm diameter by 0.65cm high.

Recommendation:

1. The above cells shall be exempt from the Short Circuit Test prescribed in Enclosure 2 of NAVSEANOTE 9310. All other applicable tests shall be conducted.

Batteries comprised of active cells are manufactured by Tadiran for both commercial and military applications. None are accepted by the UL Component Recognition and Follow-Up Service. The operational temperature range for all

Tadiran active $Li-SOCl_2$ batteries is -40 to +75°C. The characteristics for four batteries are given below:

Model Number	Nominal Capacity, Ah	OCV, V	Maximum Recommended Discharge Rate, mA
TL-5386	16	3.7, 14.8	2000
TL-6614	2.5	14.8	1000
TL-5307	0.7	7.4	15
TL-5306	0.7	11.1	15

Notes: 1. Model TL-5386 is the Tadiran $Li-SOCl_2$ version of the U.S. Army's BA-5598/U. The TL-5386 battery is comprised of four series-connected prismatic cells each of which incorporates a vent designed to open at about 150 psi (1034 kPa). A diode is electrically connected in parallel with each cell to alleviate some of the hazards attendant with forced overdischarge. Each positive lead (i.e., $+A_1$ and $+A_2$) is equipped with a replaceable 3A electrical fuse. The dimensions for this battery are 11.9cm high x 5.24cm wide x 9.05cm thick.

2. The model TL-6614 battery is cylindrical with a diameter of 3.63cm and 10.1cm high (i.e., a stack four half D cells). This battery does possess a venting mechanism.

3. Models TL-5307 and TL-5306 are dimensionally the same as the NEDA L1604 battery: 4.93cm high by 2.62cm wide x 1.75cm thick. Model TL-5307 is comprised of two TL-2150 cells electrically connected in series; model TL-5306 is comprised of three TL-2150 cells electrically connected in series.

<u>Recommendation</u>: Tadiran batteries, such as those given above, shall be subjected to <u>all</u> applicable tests prescribed in Enclosure 2 of NAVSEANOTE 9310.

Tadiran also specializes in the design and production of reserve $Li-SOCl_2$ cells and batteries for the military and aerospace community. All production units submitted for U.S. Navy applications shall be subjected to the specialized safety test program given in NAVSEAINST 9310.1B.

Union Carbide Corporation

Union Carbide currently manufactures a one Ampere hour non-standard Li-$SOCl_2$ cylindrical cell, Model L31, which constitutes the basic unit for cell models L1001 (L31 cell with plastic jacket) and L1002 (L31 cell with plastic jacket and welded tabs). Two L31 cells connected in series comprise the L722 battery (NEDA L1604). The L31 cell is slightly smaller (1.33 cm diameter, 4.6 cm height) than the ANSI standard AA cell (1.45 cm diameter, 5.05 cm height) and weighs about 14 grams. Other features include a bobbin cell design with a centrally located lithium anode, a crimp seal, and a blowout vent mechanism in the cell top which releases at internal pressures of 400 to 600 psig (2760 to 4150 kPa). The L31, L1001, and L1002 cells as well as the L722 battery do not possess electrical or thermal fuses. The three cell models have been accepted by the Underwriters Laboratories (UL) Component Recognition and Follow-Up Service.[11D]

Union Carbide L31, L1001, and L1002 cells will vent at temperatures between 70 and 160°C when subjected to short circuit testing, to forced overdischarge and charge conditions at excessive current levels (i.e., current rates greater than the recommended maximum discharge rate of 0.1A), and to several thermal abuse conditions. No cell explosions were reported by either UL or Union Carbide.

Recommendations:

1. Total containment of all cell contents is mandatory for cell or battery use in such critical applications as those encountered aboard submarines or in aircraft cockpits. Each undischarged (fresh) cell contains approximately 3.0 to 3.5 grams of highly toxic $SOCl_2$.
2. The L31, L1001, and L1002 cells and batteries comprised of these cells shall be exempt from the testing prescribed in Enclosure 2 of NAVSEANOTE 9310, with the exception of the High Temperature Test, provided that the General condition and the applicable Specific condition(s) given below are met:
   a) General condition: 1) The operational temperature shall be less than 70°C, and 2) The discharge rate for a cell or series string of cells shall be less than or equal to the recommended maximum rate of 0.1A.

b) Specific conditions: 1) a cell or single series string of cells used as a sole source or power shall incorporate an appropriate, low current value (e.g., 0.5A) electrical fuse in the negative (ground) leg.

2) A single series string of cells used as a sole source of power shall, in addition to 1), above, incorporate a thermal fuse designed to open at temperatures of 89 to 95°C. This fuse shall be located between adjacent cells or in the geometric center of a group of cells.

3) Batteries to be used as sole power sources which are comprised of cells or series strings of cells electrically connected in parallel shall incorporate blocking diodes in the positive leg to prevent the electrical charging of a depleted cell or series string of cells, respectively. Appropriate electrical and thermal fusing shall also be required for these batteries.

4) Cells and batteries which serve as backup power supplies to a mains power supply shall, in addition to the applicable electrical and thermal safety features (above), incorporate redundant diode protection. Such protection may also be achieved through use of either an electrical fuse or a resistor located between a single diode and the mains power supply. It is important to note that the values for either the fuse or the resistor should be selected to limit the charging current to less than 10 mA in the event of diode failure.

Lithium-Thionyl Chloride Medical Cells

Lithium-thionyl chloride (Li-$SOCl_2$) AA and ½AA medical cells, developed by Arco Medical Products, were first utilized as power sources for implantable cardiac pacemakers in August, 1974. However, these cells exhibited low realized capacities when discharged at typical pacemaker current levels of about 15 to 35 microamperes. In addition, an effective means to determine the state-of-charge or depletion status for these cells had not yet been developed. As a result, such implantable grade Li-$SOCl_2$ cells found only limited use. Within the past five to ten years, several implantable devices have been developed which require cells or batteries to possess higher power capabilities than can be achieved by the very reliable lithium-iodine (Li-I_2) cardiac pacemaker cell system. These applications include insulin/drug infusion pumps, automatic defibrillators, neurological stimulation devices for pain control, and programmable pacemakers.

Medtronic/Energy Technology and Wilson Greatbatch Ltd. both manufacture specially designed Li-$SOCl_2$ cells to fulfill the power requirements of devices such as those given above. All cells are of a non-standard shape and size in order to conform to the spatial requirements of the implantable devices. Typically, these cells are D-shaped with a total length measurement extending from the centerpoint of the semicircular end to the top of the cell case. The diameter of the semicircle is equivalent to the cell width. These cells feature prismatic internal construction, glass-to-metal seals, and low self-discharge rates. None of the cell models from both manufacturers possess mechanical vents or electrical/thermal fusing. The characteristics for each manufacturer's cells are discussed separately.

A. Medtronic/Energy Technology In addition to the characteristics described above, Medtronic Li-$SOCl_2$ cells feature a ribbed carbon electrode structure designed to limit the contact surface area with the cell case (case positive polarity) and an operational temperature range of +37 to +60°C. The characteristics for two Medtronic cells are given below:

Model Number	Cell Weight, g	Nominal Capacity, Ah	Maximum Recommended Discharge Rate, mA
ALPHA 36T	15.6	2.26	10
MIREL T	17.9	2.64	10

NOTES: 1. Dimensions for ALPHA 36T are: 3.6 cm long x 2.74 cm wide (also the diameter of semicircular end) x 0.8 cm thick; dimensions for MIREL T are: 2.4 cm long x 4.8 cm wide (also the diameter of semicircular end) x 0.9 cm thick.

2. The maximum constant current levels required for most medical applications are 2.0 mA and 1.6 mA for the ALPHA 36T and MIREL T cells, respectively. Some applications require pulse current levels of up to 1.5 A for periods ranging from less than a millisecond to several seconds.

3. The anodes in Medtronic cells may be composite structures of pure lithium metal surrounding an inner element consisting of an alloy of the intermetallic compound, Li_2Ca, and a calcium-saturated lithium phase. The incorporation of this anode in Medtronic cells provides a means to determine the state-of-charge toward the end of useful (i.e., load voltages above 3.0V) discharge.

4. Medtronic cells may also possess lithium anodes, as described in 3, above, which are coated with a cyanoacrylate polymer. This coating is thought to reduce self-discharge during storage and to give added isolation between electrode elements.

5. Cells which correspond dimensionally with the Model ALPHA 36T cell were subjected to the electrical abuse tests of short circuit, forced overdischarge, and charge. No thermal abuse tests were conducted. The results of the electrical abuse tests are summarized below:

   a) Short circuit tests: No ventings or explosions were observed for fresh and partially discharged cells short circuited through a five milliohm load at 37°C and at room temperature.

   b) Forced overdischarge: No ventings or explosions were observed for cells forced into cell voltage reversal at rates as high as 60 mA for up to nine hours at initial temperatures of 37°C and room temperature. Cells did exhibit temperature increases of 60 to 70°C when forced overdischarged at the 60 mA rate at 37°C. In addition, case bulging occurred at overdischarge rates of 30 and 60 mA.

   c) Charging: No ventings or explosions were observed for cells charged for eight hours at 21 mA at 37°C. The temperature increase was only 2°C but some case swelling occurred.

Recommendation: It is unlikely that these Medtronic cells will be considered for any present U.S. Navy applications other than those directly related to medical implantation. However, future military applications may require a Medtronic Li-$SOCl_2$ cell or battery incorporating a reliable state-of-charge indicator. Should this need arise, a recommendation to subject cells or batteries to the electrical abuse tests prescribed in Enclosure 2 of NAVSEANOTE 9310 will depend upon operational conditions. In any case, the High Temperature Test given in Enclosure 2 of NAVSEANOTE 9310 shall be conducted for any candidate power supply comprised of the Medtronic cell(s).

B. Wilson Greatbatch Ltd. Greatbatch manufactures both Li-$SOCl_2$ and Li-BrCl in $SOCl_2$ cells for use in implantable devices. These cells feature negative case polarity and an advertized operational temperature range of -40 to +72°C. The characteristics for several cell models are given below:

Model Number	Cell Weight, g	Nominal Capacity, Ah	Maximum Recommended Discharge Rate, mA
8403	18	2.2	12
8404	21	2.5	12
8071	18	1.7	12
8072	28	2.6	12
8201	21	1.8	12
8310	21	1.9	12

NOTES:

1. Cell models 8403 and 8404 contain only $SOCl_2$ as the cathode material; all other cell models contain BrCl in $SOCl_2$ as the cathode material.
2. Dimensions for cell models 8201, 8310, and 8404 are: 4.5 cm long x 2.3 cm wide (also the diameter of the semicircular end) x 0.86 cm thick; dimensions for cell models 8071 and 8403 are: 4.5 cm long x 2.8 cm wide (also the diameter of the semicircular end) x 0.7 cm thick; dimensions for cell model 8072 are: 7.0 cm long x 2.9 cm wide (also the diameter of the semicircular end) x 0.7 cm thick.
3. The normal discharge rate for all cells listed above is 0.35 mA.

Recommendation: Little safety related data are available which detail the behavior of these cells when subjected to electrical and thermal abuse testing.

The advertized operational temperature range of -40 to +72°C implies that these cells are available for use in commercial and military applications in addition to specific medical devices. In the event that these cells are proposed as power sources for U.S. Navy applications, a recommendation to require electrical abuse testing in accordance with Enclosure 2 of NAVSEANOTE 9310 will depend upon actual cell or battery operational conditions and requirements. All cells and batteries for U.S. Navy military use shall be subjected to the High Temperature Test prescribed in Enclosure 2 of NAVSEANOTE 9310.

Manufacturers:

1. Active cells and batteries for commercial or military applications:

   Altus Corporation
   Eagle-Picher Industries, Inc.
   Electrochem Industries
   GTE Products Corporation
   Hellesens Battery Engineering, Inc., Battery Engineering, Inc., A/S Hellesens
   Power Conversion, Inc.
   SAFT America, Inc.
   Tadiran Israel Electronics Industries Ltd.
   Union Carbide Corp., Battery Products Div.

2. Active cells for medical applications:

   Arco Medical Products
   Medtronic/Energy Technology
   Wilson Greatbatch Ltd.

3. Reserve batteries or Specialty cells and batteries:

   Altus Corporation
   Eagle-Picher Industries, Inc.
   GTE Products Corporation
   Hellesens Battery Engineering, Inc., Battery Engineering, Inc.
   Honeywell, Inc.
   Tadiran Israel Electronics Industries Ltd.

Toxicity: Thionyl Chloride ($SOCl_2$) will decompose to highly toxic HCl and SO_2 fumes on contact with moist air. Sulfur dioxide (SO_2) concentrations of 500 ppm are considered to be immediately dangerous to life; while concentrations of 50 to 100 ppm are the maximum permissible concentration levels for exposure of 30 to 60 minutes. Sulfur dioxide will, in turn, react with moist air to form sulfurous acid, H_2SO_3, which slowly converts to sulfuric acid, H_2SO_4. Sulfur dioxide is also produced as a reaction product in thionyl chloride cells. Hydrochloric acid (HCl) concentrations of 1000 to 2000 ppm are highly toxic and will cause severe respiratory distress. Aluminum chloride ($AlCl_3$) is a moderate toxicity hazard which will, however, react with water to produce highly toxic HCl fumes. Bromine chloride (BrCl), the interhalogen additive in Electrochem Industries' BCX cells, will decompose at elevated temperatures, emitting highly toxic chlorine (Cl_2) and bromine (Br_2) fumes. Exposure to high concentrations of Cl_2

and Br_2 may cause pulmonary edema.

Flammability: Bromine chloride (BrCl) is a moderate fire hazard by spontaneous chemical reaction. Sulfur (S), a discharge product in the cell reaction, is a slight fire hazard when heated. The sulfur oxide product, SO_x, is highly toxic.

OTHER PRIMARY LITHIUM BATTERY SYSTEMS

Lithium-Aqueous Electrolyte Systems[74-77]
Li-O_2, Li-H_2O_2, Li-Ag_2O_2, Li-H_2O

The major safety concern relative to all the lithium-aqueous battery systems is the creation of thermal runaway conditions due to electrolyte leakage into a cell stack at open circuit. Fires and/or explosions would then result. Since all lithium-aqueous batteries consist of large, high power custom modules, testing in accordance with Enclosure 2 of NAVSEANOTE 9310 would be impractical.

Recommendation: Worst case conditions would occur when electrolyte inadvertently enters a cell stack under open circuit or under internal short circuit conditions. Each of the above would create rapid temperature increases with the production of large amounts of hydrogen. The net result would be a fire and/or a hydrogen explosion. It is recommended that batteries be subjected to shock, vibration, and drop testing to ensure that the integrity of the cell stack and its components will remain under the most severe handling conditions.

Manufacturer: Gould Ocean Systems Division under license from Lockheed.

Toxicity: Silver compounds cause skin pigmentation (argyria)
H_2O_2 will cause burns

Flammability: H_2O_2 is a fire and explosion hazard
Hydrogen is flammable in concentrations of 4 to 18% (volume), explosive in concentrations of 18 to 78%

Lithium-Copper Sulfide[78-80]
Li-CuS

Lithium-copper sulfide cells and batteries were first produced at one time by E.I. duPont de Nemours, SAFT, and Cordis (pacemaker cells). At one time, Ray-O-Vac Corporation manufactured a nine volt NEDA L 1604 battery for military applications. Presently, Ray-O-Vac hand manufactures the Lithium 2001 experimental cell only on a contract basis for the U.S. military. This cell weighs 10 grams and contains about 0.3 gram of lithium. The rectangular cell is 4.2 cm long x 2.3 cm wide x 0.38 cm thick and is of the crimp seal closure design. Typical realized capacities for this cell discharged at 25°C are 0.7 to 1.0 Ah.

Recommendations: This cell will not pose a hazard when subjected to short circuit conditions. However, the electrolyte is comprised of 1 M $LiClO_4$ in dimethoxyethane and either tetrahydrofuran or 1,3 dioxolane. Therefore, cells and batteries should be subjected to forced overdischarge and charge (if applicable) abuse testing in addition to the High Temperature Test.

Manufacturer: Ray-O-Vac

Toxicity: $LiClO_4$ will emit highly toxic chlorides when heated.

Flammability: 1,3 dioxolane and tetrahydrofuran are fire/explosion hazards in contact with heat or flame; dimethoxyethane is a moderate fire hazard

$LiClO_4$ - see General recommendation 3

Lithium-Iodine[81-83]
$Li-I_2$

The lithium-iodine ($Li-I_2$) system is an ideal power supply for such low rate applications as cardiac pacemakers and CMOS/RAM reserve backup power. A D size (prototype) prismatic cell is being developed for low rate applications (to 80 mA) requiring high reliability and long storage life. Pacemaker cells having nominal capacities of 1.5 to 3.8 Ah are available for medical applications from several manufacturers while coin shaped cells of nominal capacities of 40 to 700 mAh are available for CMOS applications from Catalyst Research Corporation. The latter $Li-I_2$ cells have been accepted by the Component Recognition Service of Underwriters Laboratories Inc.[11E]

Recommendations: Lithium-iodine pacemaker and memory backup cells shall not be required to be tested in accordance with the forced overdischarge and charge electrical abuse tests prescribed in Enclosure 2 of NAVSEANOTE 9310 provided the current level requirements of forced overdischarge and charge are not excessive. $Li-I_2$ cells and batteries will explode violently when subjected to thermal abuse or when forced discharged/charged at rates far in excess of the current capabilities for the cells. Short circuit testing shall not be required.

Manufacturers: Medical cells, Catalyst Research Corp.
Medtronics Inc.
Wilson Greatbatch Ltd.

Commercial cells, Catalyst Research Corp.

Toxicity: Iodine will emit highly toxic fumes at elevated temperatures.

Flammability: None

Lithium-Iron Sulfide Systems[84,85] Li-FeS and Li-FeS_2

Union Carbide Corporation manufactures lithium-iron disulfide (Li-FeS_2) cells in a coin configuration and batteries comprised of two or three coin cells in series. Hitachi does not offer lithium-iron sulfide (Li-FeS) cells at this time. The Union Carbide Li-FeS_2 cells contain $LiCF_3SO_3$ as the electrolyte salt with a mixture of 3-methal-2-oxazolidone, 1,3 dioxolane, and dimethoxyethane as the solvent. The following low rate Li-FeS_2 cells have been accepted by the Component Recognition Service of Underwriters Laboratories Inc. (UL):[11F]

Union Carbide model number	Nominal capacity, mAh
895	35
894	60
890	70
801	100
803	160

UL has also accepted into the Component Recognition Service batteries comprised of two model 803 and three model 803 cells connected in series, designated as L 8002 and L 8003, respectively. Short circuit testing performed by UL at 25 and 60°C showed maximum temperature increases of only 2°C and 4°C, respectively. In addition, no adverse effects were noted for cells forced discharged at current levels less than 2 mA or for cells subsequently charged at current levels below 10 mA.

Recommendation: Short circuit testing is not required for these specific cells and batteries. These cells and batteries shall not be required to be tested in accordance with the forced overdischarge and charge (if applicable) abuse tests prescribed in Enclosure 2 of NAVSEANOTE 9310 provided the application does not require current levels greater than 1 to 2 mA. At higher rates, as those required by the application, forced discharge and charge (if applicable) testing shall be performed.

Manufacturer: Union Carbide Corporation

Toxicity: little

Flammability: 1,3 dioxolane and dimethoxyethane are fire hazards.

Lithium (Lithium alloy)-Thermal Battery Systems[86-90]
Li(Al)-FeS_2 and LAN-FeS_2

The lithium-iron disulfide (Li-FeS_2 or LiAl-FeS_2) thermal battery is attaining a preeminent status among such conventional thermal systems as calcium-calcium chromate (Ca-$CaCrO_4$) as well as all other lithium thermal battery systems. Its major advantage is the ability to yield a long service life of up to an hour. This capability is many times that for the Ca-$CaCrO_4$ system. The major safety related concerns for the lithium thermal systems were given in General recommendation 2. One specific safety concern for the LAN-FeS_2 or LiAl-FeS_2 thermal battery relates to a possible thermal runaway condition as a result of the decomposition of FeS_2 to FeS and S at operating temperatures exceeding 600°C.

Recommendation: Test procedures are being developed to more accurately assess the safety characteristics for these lithium thermal battery systems. NAVSEAINST 9310.1B will contain these specific test procedures.

Manufacturers: Catalyst Research Corporation
Eagle-Picher
SAFT

Toxicity: Slight toxicity for LiCl or KCl. The eutectic mixture of LiCl and KCl will emit highly toxic chloride fumes when heated to decomposition.

Flammability: Since lithium thermal batteries may exhibit external temperatures up to 450°C, operation under test or actual conditions should not take place in the presence of combustible materials.

Lithium-Vanadium Pentoxide Systems[91-96]
Li-V_2O_5 and Li-$AgVO_x$

Lithium vanadium pentoxide (Li-V_2O_5) cells and batteries are usually custom manufactured in either the active or reserve designs to fulfill specific application requirements. In view of the above, the safety characteristics for both the active or reserve designs are not well defined. In addition to the comments given in the General recommendation 2 for reserve batteries, the Li-V_2O_5 reserve cell or battery may be inadvertently activated when the glass or thin metal ampule occupying the center volume of the cell container ruptures as a result of physical abuse. Premature activation as described above will cause the unit to heat with the possibility of venting or explosion. Instances of venting and explosions have occurred when active cells and batteries were subjected to thermal, physical, and electrical abuse conditions. Active cells in batteries are often protected by diodes to prevent voltage reversal conditions. Large active Li-V_2O_5 cells incorporate vents, fuses, and weakened areas in the case to prevent case rupture or explosion.

No safety related data have been reported for cells and batteries of the Li-$AgVO_x$ system. This implantable grade cell is designed for such medical applications as the automatic defibrillator. At the present time, Li-$AgVO_x$ cells are still being evaluated in the laboratory. This cell system contains $LiClO_4$ salt in either propylene carbonate or a mixture of propylene carbonate and dimethoxyethane as the electrolyte.

Recommendations: Cells and batteries of both the Li-V_2O_5 and Li-VO_x systems shall be subjected to the tests prescribed in Enclosure 2 of NAVSEANOTE 9310. Reserve Li-V_2O_5 cells and batteries shall be tested in accordance with the specific procedures in NAVSEAINST 9310.1B.

Manufacturers: Li-V_2O_5, Honeywell Corporation
Li-$AgVO_x$, Wilson Greatbatch Ltd.

Toxicity: V_2O_5 is highly toxic when inhaled. Methyl formate will produce toxic fumes when exposed to heat. $LiAsF_6$-moderate toxicity. $LiClO_4$ will emit highly toxic chlorides when heated.

Lithium-Vanadium Pentoxide Systems
$Li-V_2O_5$ and $Li-AgVO_x$
(cont.)

Flammability: Methyl formate electrolyte solvent is a fire and explosion hazard when exposed to heat ($Li-V_2O_5$ system). Propylene carbonate and dimethoxyethane are slight and moderate fire hazards, respectively ($Li-AgVO_x$ system).

SECONDARY LITHIUM BATTERY SYSTEMS

Lithium-Chlorine
Li-Cl_2

The lithium-chlorine secondary battery was developed in the mid-1960s at General Motors Corporation for electric vehicle propulsion applications. Additional work on the system was carried out at the Naval Ordnance Laboratory (presently NSWC) and ESB Incorporated. It was found that the technical difficulties in containing molten lithium and in producing batteries yielding consistent results were insurmountable.

Recommendation: The Li-Cl_2 system is not commercially available.

Lithium-Molybdenum Disulfide[97-100]
Li-MoS_2

Lithium-molybdenum disulfide (Li-MoS_2) secondary cells are commercially available in the ANSI A, AA, and C sizes. These spirally wound cells have attained advanced development status and, at present, feature a glass-to-metal seal as the venting device for cells subjected to severe abusive conditions. A mechanical vent in the cell case bottom is currently under development. Each C size cell also possesses an internal diode which is electrically connected in parallel with the cell to prevent cell voltage reversal under overdischarge conditions.

Large lithium-molybdenum disulfide cells are also being developed for applications requiring higher power output with higher energy densities than can be realized using nickel-cadmium or sealed lead acid cells. One such Li-MoS_2 cell (BC) is 6.6 cm in diameter, 15.2 cm in height and weighs 1 kg.

Recommendation: The A and AA size Li-MoS_2 cells and batteries comprised of these cells shall only be exempt from the Short Circuit Test prescribed in Enclosure 2 of NAVSEANOTE 9310. All other tests shall be conducted. The C and BC cells and batteries comprised of these cells shall be subjected to all tests prescribed in Enclosure 2 of NAVSEANOTE 9310.

Manufacturer: Moli Energy Ltd., Burnaby, B.C. Canada

Toxicity: Metal sulfides will react with moisture or acids to produce H_2S. When heated to decomposition, metal sulfides will produce highly toxic SO_x.

Flammability: Unknown (Proprietary electrolyte)

Lithium-Titanium Disulfide[101-108]
Li-TiS_2

Small lithium-titanium disulfide button cells were available at one time for use in miniature electronic devices such as solar rechargeable watches and calculators. These cells possessed nominal capacities of less than 100mAh. The major focus of present investigations is the development of prismatic or spirally wound cells with capacities of 5Ah to 20Ah. Such cells use an electrolyte of $LiAsF_6$ in 2-methyl-tetrahydrofuran with various additives (e.g., 2 methyl-furan).

Recommendation: In view of the fact that Li-TiS_2 secondary cells are not commercially available at the present time, no recommendation as to abuse testing can be made. However, should commercial cells be considered for future U.S. Navy applications, a program to test Li-TiS_2 cells and batteries under appropriately modified test conditions should be conducted.

Developers: Exxon Research and Engineering Co.
EIC Laboratories, Inc.

Toxicity: Metal sulfides will react with moisture or acidic media to produce toxic H_2S. When heated to decomposition, metal sulfides will produce highly toxic SO_x. Cyclic ethers emit toxic fumes when heated to decomposition.

Flammability: Cyclic ethers are flammable when exposed to heat or flames. Ethers may form thermally explosive peroxides.

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